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Determination of Oil/Water and Octanol/Water Distribution Coefficients from Aqueous Solutions from Four Fossil Fuels

B. L. Thomas

July 1984

Prepared for
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DETERMINATION OF OIL/WATER AND OCTANOL/WATER DISTRIBUTION COEFFICIENTS FROM AQUEOUS SOLUTIONS FROM FOUR FOSSIL FUELS

Thesis prepared in fulfillment
of a Master of Science Degree

B. L. Thomas

July 1984

Prepared for
Environmental Protection Agency
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Pacific Northwest Laboratory
Richland, Washington 99352

PREFACE

The growth of a synthetic fuels industry will increase the likelihood of contamination to freshwater ecological systems by coal- or shale-derived liquid products. Many fossil fuel derived organics are known to be acutely toxic to biota and some have been shown to bioaccumulate in biological tissue, becoming potentially available for food chain transfer. For example, researchers have found that polynuclear aromatic hydrocarbons (PAH) bioaccumulate in fish tissue (1-3). These contaminated fish can serve as a food source for other organisms.

Environmental consequences of widespread production and use of synthetic fuels must be better understood before these fuels go into full-scale production. Chemical characterization of constituents present in water soluble fractions (WSF) generated from fuels has been limited in scope, as have any attempts to quantify these components.

Octanol/water distribution coefficients (K_{ow}) and bituminous oil/water distribution coefficients (K_{bw}) provide a means to model the fate of fossil fuel WSF components, once they have entered an aquatic ecosystem (4). Literature K_{ow} values are not available for many energy related organic components. Additionally, available K_{ow} data for some components vary by more than an order of magnitude. Literature K_{ow} data have been determined by dissolving an amount of a single component in octanol, equilibrating this component/octanol solution with water, and measuring the concentration in one or both phases. This method of K_{ow} determination does not detect any effects a complex aqueous mixture might have upon the equilibrium behavior of the component of interest.

It was the purpose of this research project to determine both K_{ow} and K_{bw} for components present in representative synthetic and natural oils. To accomplish this, analytical methods were developed for determining many distribution coefficients from a single WSF, simulating an aquatic mixture following contamination by a fossil fuel.

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ABSTRACT

Liquid fossil fuels, both petroleum and synthetically derived oils, are exceedingly complex mixtures of thousands of components. The effect of many of these energy-related components on the environment is largely unknown. Octanol/water distribution coefficients relate both to toxicity and to the bioaccumulation potential of chemical components. Use of these partition data in conjunction with component concentrations in the oils in environmental models provides important information on the fate of fossil fuel components when released to the environment. Octanol/water distribution data are not available for many energy-related organic compounds, and those data that are available have been determined for individual components in simple, one-component octanol/ water equilibrium mixtures. In this study, methods for determining many octanol/water distribution coefficients from aqueous extracts of oil products were developed. Sample aqueous mixtures were made by equilibrating liquid fossil fuels with distilled water. This approach has the advantage of detecting interactions between components of interest and other sample components. Compound types studied included phenols, nitrogen bases, hydrocarbons, sulfur heterocyclic compounds, and carboxylic acids.

Octanol/water distribution coefficients that were determined in this study ranged from 9.12 for aniline to 67,600 for 1,2-dimethylnaphthalene. Within a compound type, distribution coefficients increased logarithmically with increasing alkyl substitution and molecular weight. Additionally, oil/water distribution data were determined for oil components. These data are useful in predicting maximum environmental concentrations in water columns.

SUMMARY

Octanol/water (K_{ow}) and oil/water (K_{bw}) distribution coefficients provide data useful in modeling the fate of organic fossil fuel components once the fuels have entered an aquatic ecosystem (4). Octanol/water distribution coefficients can be used for predicting the toxicity and the bioaccumulation potential of fuel components in aquatic systems. Oil/water distribution data can be used to determine the maximum concentrations oil components could reach in aqueous solution. Octanol/water distribution data for many energy-related organics are currently not available in the literature.

For a variety of energy-related organic compounds, methods were developed for the determination of K_{ow} and K_{bw} from aqueous solutions prepared by equilibration of different oil samples with water. Oils chosen for study included a crude petroleum oil, a petroleum distillate, a coal liquefaction product, and a shale oil. Aqueous solutions of these oils are exceedingly complex mixtures of many compound types with individual concentrations ranging from less than one μg/L to several mg/L.

To calculate K_{ow} and K_{bw}, individual compounds had to be isolated, identified, and quantified in both aqueous and nonaqueous phases. Because concentrations of many oil components were very low in both phases, trace analytical techniques were required to quantify many components of interest. Isolation schemes were developed to eliminate interfering oil components. These isolation techniques included acid-base extraction, chemical derivatization, open column chromatography, and high resolution gas chromatography (GC). Components were identified using chemical derivatization, congruency of gas chromatographic retention times of analytical standards and sample components, and gas chromatography/mass spectrometry (GC/MS).

A variety of analytical techniques were used for component analysis, depending upon the chemical species of interest. Aqueous phenols were derivatized to form their acetate esters by addition of acetic anhydride to a caustic solution. The acetate esters were quantified by GC with flame ionization detection (FID). Nitrogen bases were solvent extracted from alkaline aqueous solution and quantified by GC and nitrogen/phosphorous-specific detection (NPD). Aromatic and saturated hydrocarbons, as well as sulfur-containing heterocyclics, were solvent extracted from a slightly acidic aqueous solution. Saturated hydrocarbon fractions were isolated using silica gel chromatography with hexane as the eluant. The aromatic

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hydrocarbon fractions also contained heterocyclic sulfur compounds and were eluted from the silica gel using methylene chloride in hexane following elution of saturated hydrocarbons. Hydrocarbons, along with selected sulfur heterocyclics, were quantified by GC/FID. Aromatic hydrocarbon fractions were also analyzed by GC using a flame photometric detector (FPD) made specific for sulfur-containing compounds. Carboxylic acids were isolated by solvent extraction from an acid aqueous solution. Acids were quantified by GC/FID after derivatization to form their methyl esters using boron trifluoride/methanol.

For all component types examined in this study, except carboxylic acids, the K_{ow} data determined were independent of the kind of oil used to generate aqueous solutions and were close to values reported in the literature.

Oil/water distribution data for all compound types depended on which of the four oils was equilibrated with water. The K_{bw} of a component is controlled not only by the component's aqueous solubility but also by the composition of the oil.

Data generated during the course of this work have been added to the available K_{ow} and K_{bw} data. These studies have demonstrated the feasibility of determining distribution coefficients of a large number of compounds present in a single complex aqueous sample. They have shown that the use of literature K_{ow} data is valid in modeling environmental spills of complex bituminous fuels, and that K_{ow} data for most energy related components are not affected by the presence of other components in the sample. In this study equations were developed for relating log K_{ow} for each component type to degree of alkyl substitution.

FIGURES

TABLES

GLOSSARY

BCF	Bioconcentration factor
EPA	Environmental Protection Agency (United States)
FID	Flame ionization detection
FPD	Flame photometric detection
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectrometry
HPLC	High performance liquid chromatography
K_{bw}	Bituminous oil/water distribution coefficients
K_{ow}	Octanol/water distribution coefficients
NPD	Nitrogen/phosphorous detection
PAH	Polynuclear aromatic hydrocarbons
PBC	Prudhoe Bay crude oil
PCB	Polychlorinated biphenyls
PLOT	Porous layer open tubular
SRC II	Solvent refined coal II
TOC	Total organic carbon
WSF	Water soluble fraction
x ± y	Where x = mean and y = standard deviation

INTRODUCTION

The United States economy has become increasingly dependent upon petroleum oils as its primary source of energy. Considerable research into the practicality of converting bituminous materials other than crude petroleum into fuel oils has been conducted. At this time, however, efforts are limited primarily to bench-top studies and pilot plant operations. Alternative sources of energy include liquid and solid coal, shale formations bearing large quantities of kerogen (macromolecular organic material which can be converted to shale oil by a retorting process), and tar sands.

Previous studies concerning impacts of synthetic fuels on the environment have focused on production. Little attention has been paid to environmental concerns stemming from widespread usage of synthetic fuels. For this reason the United States Environmental Protection Agency, EPA, has sponsored a project to rank synthetic product oils according to the environmental hazard they pose (5). The EPA study is designed to assess the implications a mature synfuel industry might have upon the environment. One major EPA concern deals with the impact contamination by a bituminous material might have upon a freshwater ecosystem.

Development of synthetic fuels will be influenced by availability of capital necessary for the construction of processing facilities, governmental energy policies, and by the prices of domestic and imported crude oils. Should these factors eventually favor the production of synthetic fuels, the potential for contamination of the environment by oil products other than natural oils will increase dramatically.

Effects of petroleum spills on aqueous ecosystems have been extensively studied (6-9), but relatively little is known about environmental consequences of contamination resulting from spills of synthetic fuels. Shale oil and coal-derived oils differ in composition from natural oils in that they have much greater concentrations of components containing nitrogen or oxygen (5). Therefore, synthetic oils and petroleum oils have different chemical and physical characteristics and cannot be assumed to behave in any similar fashion in the environment.

It is important to develop the means to accurately predict ecological consequences of aqueous contamination by any oil product, natural or synthetic. To facilitate predictive modeling, a detailed chemical study of the WSF generated from each oil must be conducted. In addition, a method to estimate both toxicity and bioaccumulation potential of the individual components must be developed.

The K_{ow} and K_{bw} data for energy-related organics can be used in this predictive modeling. Karickhoff and Brown (10) have defined a K_{ow}:

$$K_{ow} = \frac{\text{component concentration in octanol}}{\text{component concentration in water}}$$

Similarly, in this study

$$K_{bw} = \frac{\text{component concentration in bituminous oil}}{\text{component concentration in water}}$$

Concentrations are expressed as concentration per unit volume in organic and aqueous phases. Thus, the resultant number is dimensionless and is frequently expressed as a $\log_{10}$ value.

The aqueous solubility of an organic component has been empirically related to its K_{ow} (11-14). Chiou et al. (12) found a linear relationship between $\log_{10} K_{ow}$ and $\log_{10}$ aqueous solubility for test compounds covering eight orders of magnitude in solubility and six orders of magnitude in K_{ow}. Thus, calculations using aqueous solubilities provide not only an estimate of additional K_{ow} data, but also a method of checking the accuracy of existing experimental K_{ow} data.

Campbell et al. (15) determined solvent/water distribution coefficients for various organic solutes for several solvents. They noted a linear relationship between log solvent/water distribution coefficients and log octanol/water distribution coefficients. Thus, if a compound's log K_{ow} is available in the literature, its distribution coefficient between other organic solvents and water can be calculated.

A considerable body of research has shown a direct proportionality between a given component's bioconcentration factor (BCF) and its K_{ow} (13, 14, 16-18) where

$$BCF = \frac{\text{component concentration in organism}}{\text{component concentration in surrounding medium}}$$

Therefore, K_{ow} data provide the means to calculate conservative estimates of component concentrations that might be expected to accumulate in biological tissues exposed to an organic contaminant. The concentration estimates are conservative because equations relating K_{ow} and BCF do not provide for mechanisms of elimination (e.g., metabolism) by the organism.

This BCF concept is especially useful when related to food chain transfer studies. Veith et al. (14) determined BCF, K_{ow}, and aqueous solubility for twenty-eight organic chemicals. They state that polychlorinated biphenyls (PCB) in aquatic ecosystems pose a greater threat to consumers of fish than to the fish populations themselves, because aqueous concentrations are apparently safe for the fish but result in accumulation of the PCBs in fish tissue to concentrations that create a hazard to consumers of the fish. Mackay (13) correlated K_{ow} data for several aromatic hydrocarbons with BCF in fish and Schultz et al. (17) related toxicity of a component empirically to its K_{ow}. Organic pollutants with log K_{ow} in the range of 2 to 6 are of the most environmental interest (10). Those with log $K_{ow} < 2$ do not partition into or accumulate in hydrophobic compartments such as the lipids contained in biological tissues. On the other hand, compounds with log $K_{ow} > 6$ tend to accumulate in any and all lipid tissue but are very sparingly water soluble.

Sorption on sediments and soils relate to K_{ow} (19, 20). In a natural ecosystem, distribution of an organic species between sediment and the aqueous phase can control aqueous concentrations of that organic chemical to which biota are exposed. Therefore, a wealth of information concerning environmental behavior of an organic species can be obtained by simply applying a few equations relating its K_{ow} to other environmental parameters of interest.

In theory, K_{ow} should remain constant regardless of the presence of other components in an experimental system and regardless of the concentrations of any other components. Data derived in a laboratory test system can be used in models predicting component fate in the environment. Literature K_{ow} data have traditionally been determined using single-component systems. This procedure is time-consuming, expensive, and does not detect the effects a complex mixture might have on equilibrium concentrations of the component of interest in the aqueous and octanol phases.

Leo et al. (21) have compiled most existing K_{ow} data into a single publication, but, unfortunately, data are simply not available for many compounds known to be constituents of natural or synthetic oils. Sources of existing K_{ow} data are frequently not in agreement (19).

To become biologically available to aquatic species such as fish, an oil component must become solubilized in an aqueous ecosystem. Literature solubility data have limitations similar to those encountered with literature K_{ow} data, in that data for many compounds are not available. A further complication arises when dealing with aqueous solubilities of oil components in the presence of the parent oil. The concentration of a given oil component in an oil WSF is a function not only of component water solubility but also of the initial oil composition. Therefore, K_{bw} calculated from component concentrations in the oil and aqueous phases for an equilibrium system provide better estimates of maximum concentrations in water, following contamination by a given quantity of oil.

Several compound classes known to be constituents of the oils studied in this research project have been examined for their toxological effects. Compound classes of particular interest to environmental chemists and toxicologists were selected for analysis in this study. Component classes chosen for study include phenols, nitrogen bases, aromatic and saturated hydrocarbons, sulfur heterocyclic compounds, and carboxylic acids.

Four oils representative of synthetic fuel technology as well as natural petroleum were chosen for study in this research project. The oils studied were:

1. Prudhoe Bay crude oil (PBC), a crude petroleum oil from the Prudhoe Bay area of Alaska. This oil is transported by pipeline to Valdez on Prince William Sound. From there it is shipped by tanker to various refineries and distribution facilities in the United States (22).

2. Number 2 fuel oil, a distillate cut with widespread usage as a fuel oil. It was this type of oil which was spilled in Buzzard's Bay, Mass., causing severe ecological damage (1).

3. Oxy, a shale oil developed by Occidental Petroleum Company. It was produced by the in situ retorting of oil shale. The production of shale oil is considered by technical experts (5) to be more economical than coal liquefaction.

4. SRC II, a 2.9 to 1 blend of medium to heavy distillate cuts produced by a pilot plant located at Fort Lewis, Washington. This process, designed to produce a low-sulfur, low-ash liquid fuel (23), involved the non-catalytic hydrogenation of pulverized bituminous coal under high temperature and pressure.

Phenolic components constitute a major percentage of the organic carbon present in coal-derived oils (24). They are also present in shale-oils (25). Data from this study show that phenols are present, to lesser extents, in the crude petroleum oil and the petroleum distillate. Nitrogen bases were chosen for analysis because they are known to be constituents of coal liquefaction and retorted shale products (16-18, 25-29). Some of these bases are also present in crude petroleum oils (30-32). Aromatic and saturated hydrocarbons are present in shale-oils (33), crude oils (34), and liquified coal products (27), and were found in all oils examined in this study. Sulfur heterocyclic compounds are constituents of both synthetically derived and natural crude petroleum oils (35, 36). Organic acids are known to constitute a large proportion of the organic carbon in by-product water created in the retorting process of shale oil (37, 38), but toxicity data is unavailable for most of these carboxylic acids. Because bioaccumulation and toxicity of components correlate with K_{ow}, it was important to quantify carboxylic acids in each oil and to determine K_{ow} data for the acids.

Phenolic compounds are more water soluble than most other compound classes examined in this study. Oil/water distribution coefficients for the more hydrophilic monocyclic phenols, phenol and the cresols, show that more than 50 percent of these components in an oil would partition into the aqueous phase upon equilibration of an oil with water at a 1:100 volume ratio. Lesser, but still very significant levels of the more highly substituted aliphatic phenols would enter the water column. Gray et al. (39) performed sequential water extractions of a coal liquid and found the rate of phenol solubilization was related to molecular weight; higher molecular weight phenols entered the water column more slowly than did phenols with lower molecular weights.

Even trace amounts of dissolved phenolic material can have detrimental effects upon water quality (40). Phenol toxicity has been studied in some detail (34, 41, 42). Rainbow trout growth was significantly reduced by phenol concentrations as low as 0.20 mg/L in the exposure water (42).

Nitrogen bases, both primary amines and heterocyclic azaarenes, are relatively polar and are, therefore, significantly water soluble. Because of their solubility, these compounds could have acute and chronic toxological effects as well as accumulate within biological lipid material. Basic components in oils have been identified as major contributors to toxic and mutagenic activity of liquid fossil fuels (26, 27, 43-45).

Shultz et al. (17) showed that toxicity of eleven selected nitrogen-containing heterocyclic compounds increased linearily with increasing K_{ow}, molecular weight, and boiling point. Southworth et al. (16) noted that both bioconcentration and acute toxicity increased with increasing molecular weight. They also found that BCFs of selected azaarenes in Daphnia pulex correlated with K_{ow}. Southworth et al. (18) studied bioconcentration of azaarenes in both fathead minnows and Daphnia pulex and found that BCFs were higher in the daphnia. They showed this observed bioconcentration deviation between species was caused by the fish's capability to metabolize the azaarenes.

Saturated and aromatic hydrocarbons are considerably less soluble in water than are the more polar phenols and nitrogen bases. Considerable toxicity testing of crude oil WSFs has been conducted, with most supporting chemistry focusing on hydrocarbon concentrations. Anderson et al. (46) studied WSF hydrocarbon concentration and toxicity to several estuarine crustacea and fish for No. 2 fuel oil as well as two selected crude oils. He determined that a WSF of either crude oil had a higher total organic carbon (TOC) concentration and contained relatively more light aliphatic and single-ring aromatics than did a WSF of the refined oil.

Aromatic hydrocarbons are believed to be potentially more toxic to the environment than are saturated hydrocarbon components (47). Normal saturated hydrocarbons with carbon numbers ranging from 9 to 24 have aqueous solubilities that decrease from 220 µg/L to less than 1 µg/L (48, 49). These extremely low solubilities keep equilibrium aqueous concentrations very low, such that little aliphatic hydrocarbon material is in aqueous solution. On the other hand, monoaromatic components, benzene and its alkyl substituted analogs, exhibit water solubilities in the mg/L range--170.5 mg/L for o-xylene and decreasing to 48.2 mg/L for 1,3,5-trimethylbenzene (50). The two-ring methyl substituted aromatic hydrocarbon, 2-methylnaphthalene, has a water solubility of about 20 mg/L (50). Thus, concentrations of the more hydrophilic aromatic hydrocarbons could reach several mg/L in the water column should an oil spill occur. Polynuclear aromatic hydrocarbons such as 3-ring phenanthrene and 4-ring pyrene, exhibit considerably lower aqueous solubilities. Giddings (27) determined that aromatic hydrocarbons containing four or more aromatic rings are practically insoluble and that even aqueous solutions saturated with such aromatics are generally not acutely toxic to aquatic organisms because hydrocarbon concentrations are very low. He found two-ring compounds are more toxic than their single-ring analogues even though they are less water soluble, and that methyl substituted naphthalene is slightly more toxic than naphthalene. DeGraeve et al. (51) studied the effects of naphthalene and benzene on fathead minnows and rainbow trout. Lower concentrations of naphthalene than benzene were required for acute toxicity. Naphthalene has a log K_{ow} of about 3.37 while the log K_{ow} for benzene is only about 2.13, so, in this case, the component with the larger log K_{OW} is more toxic. These previous studies demonstrate the importance of determining both aqueous solubility and K_{OW} for organic contaminants.

Southworth et al. (52) observed the bioaccumulation of PAH increases by nearly a factor of 10 for each ring added to the aromatic structure from a BCF of 100 for naphthalene to a BCF of 10,000 for benz(a)anthracene.

Although toxological data pertaining to sulfur-containing compounds are somewhat sparse, it has been shown that some components exhibit high carcinogenic/mutagenic activity (53, 54). The accumulation of sulfur compounds has been observed in several marine organisms following petroleum oil spills (35, 55, 56).

Data pertaining to toxological properties of organic acids are largely missing from the literature. However, carboxylic acids have been found in by-product water from shale oil production (37, 38); as a result, these acids are of interest to environmental chemists and toxicologists. In this study, concentrations of some aliphatic acids in shale oil were greater than 100 mg/L and concentrations of several of these aliphatic acids in coal-derived oil were greater than 1 mg/L. Carboxylic acids are hydrophilic and could be very important in aqueous toxological studies of fossil fuel materials.

The compound types whose toxicities have just been discussed have been analyzed by many different researchers in a variety of different substances such as oils, sediments, and biological tissues.

Phenols have been isolated from complex samples using a variety of techniques, including solvent extraction from an acidic aqueous solution (57), continuous liquid-liquid extraction from water into methylene chloride (40), silica gel column chromatography (58), and direct aqueous acetylation followed by solvent extraction (59-61). Following isolation, reversed-phase high performance liquid chromatography, HPLC (59, 62), gas chromatography, GC (40, 57-61), and gas chromatography/mass spectrometry, GC/MS (61) have been used to separate, identify, and quantify phenolic components.

Underivatized phenols are difficult to separate and quantify by GC. However, White et al. (63) used poly(ethylene glycol) and Buryan et al. (64) used tri-(2,4-xylenyl)phosphate as chromatographic stationary phases and successfully separated a variety of phenol isomers. Derivatization of phenols to heptafluorobutyrates (65), hexamethyldisilazanes (40), trimethylsilazanes (57, 66), acetates (59-61), and methyl esters using diazomethane (67) have been used prior to GC separation.

Several techniques have been used to isolate nitrogen compounds in both natural and synthetic fuel oils. Oxygen- and nitrogen-containing compounds in shale oil have been isolated using ferric chloride-clay complexation chromatography (29). Basic nitrogen compounds were isolated in one fraction while nonbasic nitrogen compounds were isolated in another following reduction with lithium aluminum hydride. Airborne nitrogen bases have been concentrated by adsorption onto Florisil filters and subsequently extracted with aqueous HCl (68). Both acid-base extraction and HPLC, coupled with GC or GC/MS, have been used to detect and quantify 2,4,6-trimethylpyridine in shale oil (25). Similar quantitative results were achieved regardless of whether HPLC or acid-base extraction techniques were used. Nitrogen bases in aqueous solutions have been concentrated using adsorption on XAD-2 microreticular resin (69) and subsequently analyzed using reversed-phase HPLC. Aromatic amines have been isolated from a coal conversion oil using cation exchange resin (26). Strong nitrogen bases from crude petroleum oils have been trapped on HCl-modified silica and subsequently purified using HPLC (31). In that study researchers were successful in isolating and quantifying triaromatic nitrogen bases such as benzo(h)quinoline and some of their alkyl analogs.

Albert (32) analyzed nitrogen compounds in petroleum using GC with nitrogen/phosphorous detection (NPD). This detector is a flame ionization detector with an alkali metal bead that is gradually volatilized so its vapors are continually present in the flame, causing the resulting flame detector to be specific for nitrogen/phosphorous. Albert assumed the phosphorous content of petroleum oils was so low that the NPD response to phosphorous was negligible and all of the response was attributed to nitrogen-containing compounds. The use of this type of compound-specific detector aids greatly in overcoming serious analytical interferences that large concentrations of hydrocarbons create.

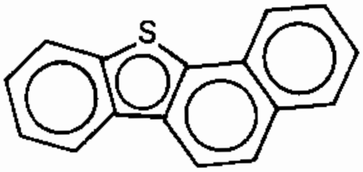
Shale oil bases have been qualitatively analyzed using porous layer open tubular (PLOT) gas chromatography for isolation and vapor phase infrared spectrophotometry for identification of components (70). These PLOT columns provided the higher capacity necessary for use with the vapor phase infrared detector that has only moderate sensitivity.

Several researchers have used GC/MS techniques for identification of nitrogen bases (24, 71-73). A high voltage (70 eV), high resolution mass spectrographic method was used successfully for identifying nitrogen- and oxygen-containing petroleum components by Peters and Bendoraitis (74). High voltage electron impact ionization produces many more ions than does lower voltage, and the high resolution permits mass and intensity measurements of up to 2000 peaks per spectrum. When alkyl pyridines and anilines are ionized using 70 eV electron impact, low resolution mass spectrometry produces nearly identical spectra, making differentiation between these two compound types very difficult. Felice (28) developed an aqueous chemical derivatization technique using acetic anhydride that could differentiate between these two compound types. In his procedure, Felice derivatized anilines and alkyl anilines to form their respective acetanilides. These derivatization products could be differentiated easily from underivatized pyridines in the sample by their changed GC retention times as well their characteristic mass spectra produced by low resolution mass spectrometry.

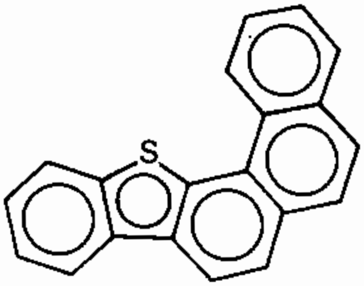
Saturated and aromatic hydrocarbons have been studied in detail by a large number of investigators using various isolation and analytical schemes. Separation of hydrocarbon compound classes; aliphatics, olefins, and aromatics, has been achieved using HPLC and a dual column system consisting of a silica gel column and a second silica gel column that had been impregnated with silver nitrate (75). Alkanes in shale oil have been analyzed by vapor phase reaction/gas chromatography utilizing a precolumn reactor of sulfuric acid supported on diatomite (33). The precolumn reactor removes alkenes, aromatics, and oxygen-, nitrogen-, and sulfur-containing species from the sample yielding a clean alkane sample. Analysis of gasoline has been accomplished by high resolution GC (76). Shale oil hydrocarbons have been examined by preparative liquid chromatography followed by glass capillary gas chromatography (77). Warner (78) developed a method to quantify aromatic hydrocarbons in biological tissues using silica gel chromatography followed by capillary GC.

Researchers have expressed considerable interest in analyzing sulfur-containing heterocyclic fractions of various oils. Characterization of these components is important because many are suspected carcinogens and/or mutagens (53). Further, health effects are related to structure. For example, benzo(b)naphtho(2,1-d)thiophene is noncarcenogenic while benzo(b)phenanthro(3,4-d)thiophene, a structurally related molecule, is a very potent carcinogen (54) (see page 10).

A variety of isolation and quantification schemes have been used for analysis of sulfur-containing heterocycles. Because individual component concentrations are quite low, Later et al. found it necessary to use SRC II samples as large as 10 grams for analysis of sulfur-containing components (79). Initial fractionation of a coal-derived liquid to isolate a sulfur heterocyclic/aromatic hydrocarbon fraction has been accomplished using a polar HPLC column and solvent programming to elute components in order of



Benzo(b)naphtho(2,1-d)thiophene



Benzo(b)phenanthro(3,4-d)thiophene

increasing polarity (80). Solid coal has been pulverized and solvent extracted in a soxhlet extraction apparatus with benzene (81). This benzene extract was then reduced to dryness and subsequently refluxed in cyclohexane to solubilize aromatic hydrocarbon and heterocyclic sulfur components. Sulfur-containing components were isolated from the aromatic hydrocarbons using a clay-gel percolation procedure.

Sulfur-containing components have been isolated from aromatic hydrocarbons through oxidation of the sulfur species with hydrogen peroxide to form the corresponding sulfones (53, 54, 79). These sulfones can be separated from the bulk of the aromatic hydrocarbons by silica gel chromatography and subsequently reduced to sulfides with lithium aluminum hydride. Repurification of the reduced sulfur species yield samples free from interfering hydrocarbons.

Sulfur components have also been isolated from biological tissues (57) and sediments (36). In sediment sample extracts, subsequent removal of elemental sulfur was necessary before analysis could proceed. Blumer (82) used a sulfur removal procedure involving percolation of the sample through a column of active copper powder that reacts with elemental sulfur at room temperature, removing it from sample components.

High resolution GC using flame photometric detection (FPD) has frequently been used to quantify individual sulfur components (53, 54, 81). Individual components have also been positively identified through use of GC/MS (36, 79, 83). Flame photometry is a useful detection technique for sulfur components because of its specificity. However, its response is not always linear (53) and varies with oxygen/hydrogen flow ratios (84) so caution must be exercised in its use for quantification.

Yet another identification technique is that of high resolution mass spectrometry (85) which produces a very characteristic spectrum for each component. This method has the advantage of eliminating time consuming sample preseparation procedures designed to remove interfering hydrocarbons.

Organic acids have been isolated and analyzed using a variety of techniques. Acids from oil shale retort water (37) and other complex aqueous samples (86) have been isolated using resin adsorption. Phenol acids have been isolated using silica gel chromatography (87). A common means to isolate acids from aqueous media involves acidification to pH 2 and solvent extraction (88, 89).

Separation of isolated acid fractions has frequently been accomplished using HPLC (37, 90, 91). Gas chromatography has also been a widely used technique for the analysis of carboxylic acids. However, because underivatized acids do not separate into distinct peaks on nonpolar GC columns, a variety of derivatization techniques have been used including esterification by reaction with boron trifluoride in methanol (38, 88, 89), boron trifluoride in butanol (37), and diazomethane (86). Silyl derivatives have been prepared using an N,O-Bis(trimethylsilyl)acetamide-acetronitrile solution (87). In addition to these techniques, azeotropic sulphuric acid-catalyzed reaction (92, 93), and reaction with tetramethyl ammonium hydroxide/methanol/methyl iodide/n-butyl acetate solution (94) have resulted in esterification. Methyl esters of carboxylic acids have then been analyzed using GC (79, 92, 93) and GC/MS (38, 86, 87, 94).

APPROACH

Each of the oils chosen for examination in this study is an exceedingly complex mixture made up of thousands of different components that differ widely in their concentrations, polarities, and toxicities. Analytical methodologies developed for analysis of each oil and its WSF must be able to accommodate low-level concentrations of components of interest in the µg/L range while providing a means to remove interfering components that are often present in much higher concentrations. In many cases components of interest possess physical and chemical characteristics similar to those of interfering components, thus making isolation difficult. Isolation and analytical schemes were based on a common physical characteristic of all components within a compound class. Acidic components were solvent extracted from acidic aqueous solutions, and basic components were extracted into an organic solvent from caustic solution. Neutrals were isolated by silica gel chromatography. High resolution capillary gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) were used to further isolate, identify, and quantify specific components. Further, specific GC detectors were used to detect and nitrogen and sulfur-containing components. Sulfur compounds were detected using flame photometry (FPD) and nitrogen compounds were detected with a nitrogen/phosphorous specific detector (NPD).

Quantitative data of components in oil, octanol, and aqueous phases provided information necessary to calculate K_{ow} and K_{bw}.

ANALYTICAL METHODS

The following section describes the analytical procedures developed in this study and discusses the rationale for choosing those specific methods. A section is devoted to the generation of oil, octanol, and WSF samples. Analytical methods developed for each compound type differ considerably, so individual sections deal with analysis of each compound type and the specific problems encountered in the isolation and quantification of the compounds. A final section deals with reagents, supplies, and instrumentation for all compound types.

GENERATION OF WSF

Separate water soluble fractions were generated for each compound type within each oil. All samples were generated at 22 ± 1°C. For all compound types except phenol, WSFs were generated using a 10:1 (v:v) ratio of water to oil. Phenols were studied on WSFs prepared from 100:1 water to oil ratios. The 10:1 WSFs were generated by shaking 157.5 mL deionized, distilled water and 17.5 mL oil in a 150 mL Corex® brand centrifuge tube capped with a foil-lined screw cap on a rotary shaker at 200 rpm for a 16-hour period.

Anderson et al. (46) equilibrated petroleum oils with artificial seawater and analyzed the water phase at different times during the preparation. Their results indicated that bacterial contamination affected aqueous hydrocarbon concentrations with mixing times longer than 29 hours. They found optimal hydrocarbon extraction with minimal bacterial contamination for mixing times of about 20 hours. The 20-hour equilibration time was shortened to 16 hours for this study to allow workup of aqueous samples in a single day. Because Oxy is viscous at room temperature, an experiment was done to verify that a 16-hour equilibration period was adequate to generate an Oxy equilibrium WSF in this study. Oxy carboxylic acids were analyzed after both 16- and 36-hour equilibration times. Acid concentrations in a 16-hour WSF were not statistically different from those in a 36-hour WSF (Table 1). Phenols were analyzed in aqueous phases resulting from both 16- and 36-hour equilibration times of SRC II with water. Results are tabulated in Table 2 and demonstrate that a 16-hour shaking period is adequate to establish an equilibrium SRC II WSF.

Six replicate samples were generated for each analysis. After the samples were shaken, they were centrifuged at 3000 rpm for 20 minutes to

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TABLE 1. Concentrations of Oxy Aqueous Phase Acids after 16 and 36 Hours Equilibration (μg/mL)

Component	16 Hour (n = 3)	36 Hour (n = 3)
Hexanoic acid	0.6 ± 0.1	0.8 ± 0.0
Heptanoic acid	2.5 ± 0.4	3.1 ± 0.1
Octanoic acid	7.5 ± 0.8	8.6 ± 0.6
Nonanoic acid	8.1 ± 0.8	7.6 ± 2.0
Decanoic acid	4.3 ± 0.4	3.2 ± 1.5
Undecanoic acid	0.5 ± 0.1	0.4 ± 0.1

ensure complete separation of oil and water phases. Oil phases were removed by means of Pasteur pipettes to clean vials fitted with Teflon®-lined caps. Aqueous phases were carefully siphoned with a 15-cm length of narrow-bore Teflon® tubing into 250-mL graduated cylinders for volume measurement. Three replicate aqueous samples were subjected to extraction for the compound type of interest. The other three replicates were returned to clean centrifuge tubes for equilibration with 0.5 mL n-octanol, purified by an EPA procedure (10). Octanol/water systems were equilibrated, centrifuged, and siphoned in a manner analogous to that used for oil/water systems.

A representative test component from each compound type was chosen to test the ability of each analytical method to generate K_{ow} data comparable to literature values. Test compounds were weighed and dissolved in octanol. A 0.5-mL portion of this octanol solution was equilibrated with 150 mL distilled water in a manner analogous to that used for WSF generation. Samples were siphoned, centrifuged, and subjected to the appropriate analytical procedures. Pure compound experiments were conducted at concentrations in each phase of several mg/L; experiments with fossil fuel WSFs often involved analysis of individual components at concentrations much lower, often at the μg/L range. Blanks were generated and analyzed in this same fashion. High concentrations of test compounds were used in this experiment to ensure that any deviation of K_{ow} from

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TABLE 2. Concentrations of SRC II Aqueous Phase Phenols After 16 and 36 Hours Equilibration (μg/mL)

Component	16 Hour (n = 3)	36 Hour (n = 4)
Phenol	360 ± 13	370 ± 17
o-Cresol	150 ± 3.5	160 ± 5.5
m-Cresol	400 ± 6.7	400 ± 15
p-Cresol	220 ± 1.3	220 ± 10
C_2 Phenol	7.5 ± 0.89	7.6 ± 0.48
2,6-Dimethylphenol	28 ± 0.8	27 ± 0.7
2,4-Dimethylphenol	50 ± 0.9	49 ± 1.2
C_2 Phenol	72 ± 1.3	70 ± 2.6
m-Ethylphenol	150 ± 0.4	140 ± 8.7
2-Isopropylphenol + p-Ethylphenol + 3,5-Dimethylphenol	130 ± 5.6	120 ± 10
3,4-Dimethylphenol	50 ± 0.4	47 ± 4.0
2,4,6-Trimethylphenol	12 ± 0.2	11 ± 1.1
C_3 Phenol	11 ± 0.7	10 ± 0.9
C_3 Phenol	15 ± 0.5	13 ± 1.1
C_3 Phenol	20 ± 0.7	19 ± 1.7
2,3,6-Trimethylphenol	47 ± 0.4	43 ± 4.8
C_3 Phenol	67 ± 0.9	62 ± 6.4
C_3 Phenol	13 ± 0.4	12 ± 0.9
C_4 Phenol	4.2 ± 0.06	4.0 ± 0.36
C_4 Phenol	5.5 ± 0.12	5.3 ± 0.34
C_4 Phenol	3.4 ± 0.04	3.2 ± 0.24
Indanol	85 ± 3.3	82 ± 7.2
C_5 Phenol	3.4 ± 0.43	2.8 ± 0.30
C_5 Phenol	13 ± 0.7	12 ± 0.9
C_1 Indanol	9.6 ± 1.41	10 ± 0.8
C_5 Phenol	9.1 ± 0.57	8.3 ± 1.07
Total	1940 ± 27	1910 ± 69

literature values could be attributed to analytical scheme failure. At very low component concentration, adsorption to container surfaces becomes relatively more important, and poor integration of peak area in quantification could result in inaccurate data.

PHENOLS

The analytical approach followed in this study, a slight modification of a procedure developed by Bean et al. (61), is outlined in the flow diagram in Figure 1. Aqueous samples (50 mL) were made 0.1 N basic by the addition of NaOH. Three hexane extracts served as washes to free the sample of basic and neutral components. A single hexane wash was found to be inadequate for the removal of hydrocarbons and octanol, both of which

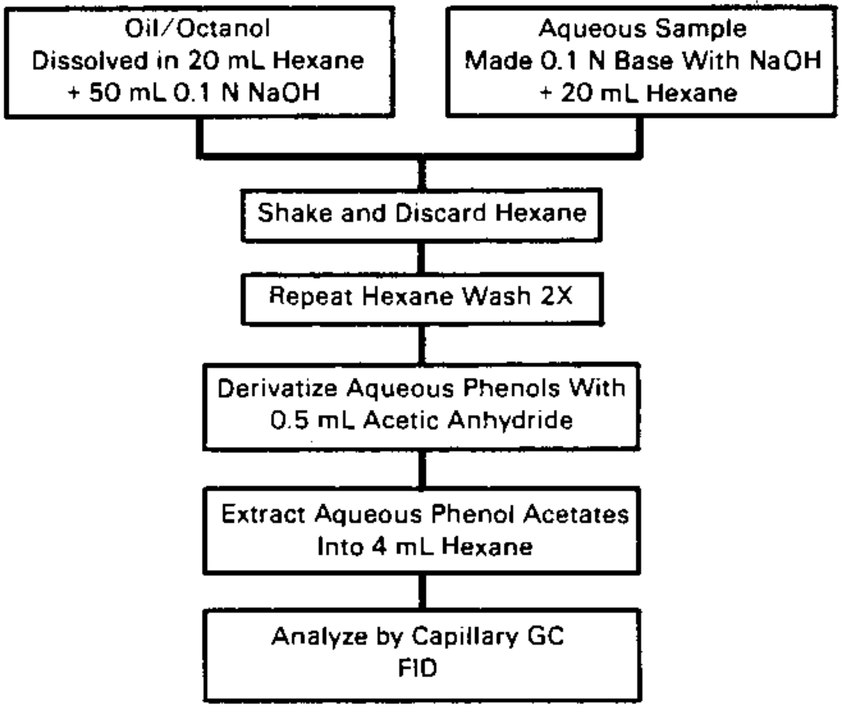

FIGURE 1. Flow Chart for Analysis of Phenols

were present in quantities sufficient to invalidate the analysis. Three extracts, however, did serve as an effective clean-up step. Aqueous phenols were then derivatized by adding 0.5 mL acetic anhydride to form the phenol acetates. Excess acetic anhydride hydrolyzed to acetic acid. Following derivatization the measured aqueous pH was 5 or 6, thereby stabilizing the phenol acetates. The acetates were extracted into 4 mL hexane. Phenols in the octanol and oil phases were extracted into 0.1 N NaOH. The three hexane washes were performed, the samples were derivatized, and then the acetates were solvent extracted. An aliquot of n-dodecane in hexane was added as internal standard and the samples were quantified by GC using FID. Various phenol standard compounds were subjected to the analytical procedure, and their response factors relative to that of the internal standard were calculated. This method of calibration provided correction for chemical and mechanical losses during the sample workup procedure. The method was calibrated both for phenols in oil/octanol and for aqueous phenols using phenol standards dissolved in methanol. For determination of response factors for oil/octanol samples, an amount of standard in methanol was added to a solution of 0.5 mL octanol and 20 mL hexane. The octanol/hexane solution was then subjected to base extraction and the three subsequent hexane washes used for sample isolation. Determination of response factors from aqueous solution was accomplished through addition of the standard compounds in methanol solution directly to the aqueous base, followed by the three hexane washes. Differences in relative response factors determined for aqueous and oil/octanol phenols are judged negligible. Using this procedure with only one hexane wash of aqueous phenols, Bean et al. (61) found phenol recoveries range from 71 to 90 percent for alkyl substituted phenols. Relative response factors determined, using the analytical scheme with only one hexane wash, differed only very slightly from those when three hexane washes were performed. Therefore, losses due to the additional solvent washes are judged minor. Both relative response factors derived for aqueous phenols and those for oil/octanol phenols, as well as the overall mean values, are tabulated in Table 3.

The GC/MS identification of phenolic components was done on an SRC II WSF and gave results similar to those in another study (61). Mass spectrometry was useful for identification of phenolic compounds with varying degrees of aliphatic substitution but did not allow the

TABLE 3. Phenol Relative Response Factors

	Relative Response Factors		
Component	Aqueous (n = 3)	Oil/Octanol (n = 3)	Mean (n = 6)
Phenol	1.994 ± 0.032	2.107 ± 0.115	2.051 ± 0.097
p-Cresol	1.371 ± 0.011	1.408 ± 0.032	1.390 ± 0.030
3,4-Xylenol	1.228 ± 0.009	1.257 ± 0.013	1.242 ± 0.019
2,3,5-Trimethylphenol	1.391 ± 0.025	1.491 ± 0.009	1.441 ± 0.057
5-Indanol	1.260 ± 0.008	1.291 ± 0.005	1.276 ± 0.018
1-Naphthol	1.507 ± 0.009	1.530 ± 0.016	1.519 ± 0.017

identification of specific positional isomers. Phenol acetates give very characteristic spectra with the base peak being 42 amu less than the molecular ion, corresponding to the loss of ketene, $CH_2=C=O$. This loss gives an ion corresponding to the underivatized phenol. Figures 2 and 3 show mass spectra derived from phenol acetate and a representative dimethyl phenol acetate isolated from an SRC II WSF generated in this study.

Phenol positional isomers of equivalent molecular weights were not differentiated by GC/MS spectra. Insofar as standard aliphatic substituted phenols were available, tentative identifications of specific isomers were made based on congruency of chromatographic peaks of unknown components and peaks of standard compounds that had been derivatized to form phenol acetates. Those tentative identifications were reinforced using work of Mattsson and Petersson (66), who determined relative retention times of silyl derivatives of phenols. Component separation on a nonpolar column is

```
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File type = linear
Base Peak =  94.00  Base Peak Abundance =     2302  Total Abundance =     4148
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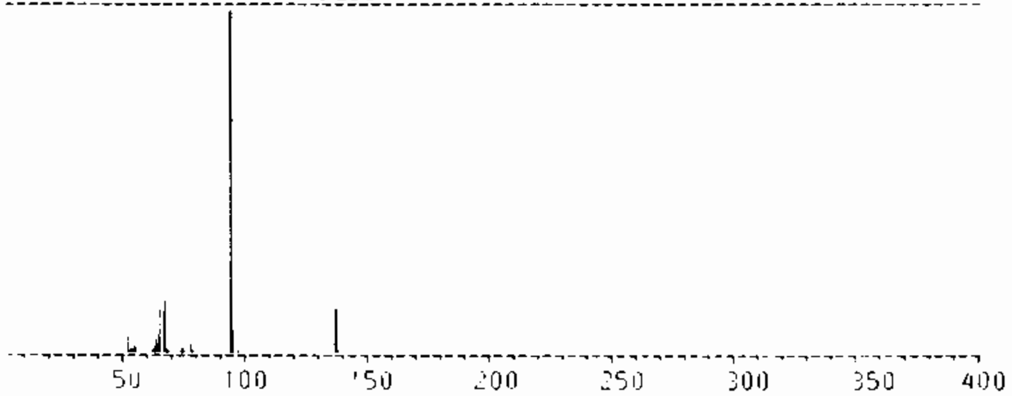

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Lower Abundance Cutoff Level =    2.0%
  MASS     ABUNDANCE (%)          MASS    ABUNDANCE (%)          MASS    ABUNDANCE (%)
 51.00         4.6               66.00       17.0               95.00        6.3
 63.00         4.2               77.00        2.5              136.05       13.2
 65.00        12.5               94.00      100.0
```

FIGURE 2. Spectrum of Acetylated Phenol

```
** Spectrum #  9 **  Sample #      1   Retention Time =22.32 minutes
Scanned from  50 to 400 amu  Number of Peaks Detected =  100
File type = linear
Base Peak = 122.05  Base Peak Abundance =     1137  Total Abundance =     3342
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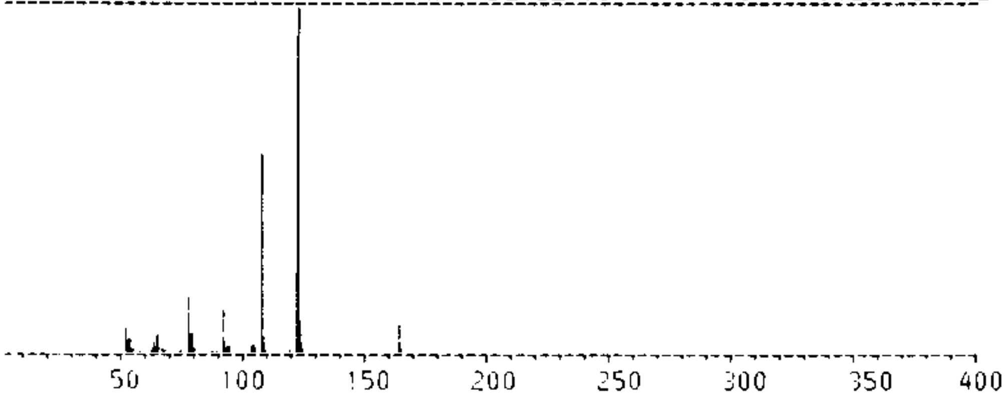

```
Lower Abundance Cutoff Level =    2.0%
 MASS     ABUNDANCE (%)          MASS    ABUNDANCE (%)           MASS    ABUNDANCE (%)
 51.00         7.2               78.00       4.9                108.05        4.5
 52.00         3.2               79.00       5.4                121.15       23.3
 53.00         3.9               91.00      12.3                122.05      100.0
 63.00         3.1              104.05       2.6                123.05        9.1
 65.00         5.1              107.05      57.3                164.05        8.0
 77.00        15.9
```

FIGURE 3. Spectrum of Acetylated Dimethylphenol

primarily due to differences in boiling temperatures of various compounds. Using relative retention times of phenol silyl derivatives to identify acetate derivatives requires the assumption that boiling temperatures of silyl derivatives follow the same trends with alkyl substitution as do those of acetate derivatives.

Compounds not specifically identified were classed according to the number of carbons attached to the ring as substituents. Methyl substitution is designated as C_1, ethyl or dimethyl as C_2, etc.

Precision of the method using the standard compound, o-cresol, was less than 5%. In a 50-mL aqueous sample, 10 ng/mL of o-cresol was easily determined. The ability of this method to accurately determine concentrations in oil, octanol, and water phases necessary for the determination of accurate K_{ow} was tested by dissolving o-cresol in octanol and subsequently equilibrating triplicate aliquots of this octanol solution with water and analyzing both phases. Triplicate analyses yielded a log K_{ow} of 2.04. This compares well with a literature K_{ow} of 1.95 (21) and with values determined from the fossil fuels in this study.

NITROGEN BASES

Analysis of nitrogen bases in this study used a combination of several of the techniques listed in the introductory section. Isolation of nitrogen compounds used acid/base extraction and was thus limited to nitrogen bases--pyridine, aniline, quinoline, and isoquinoline--and their alkyl analogs. Very weak bases and neutral nitrogen compounds were excluded by the analytical method developed for this work.

Figure 4 shows the flow diagram of nitrogen base isolation. Briefly, the method involved two 25-mL methylene chloride solvent extracts of an aqueous oil solution made 0.1 N acid by addition of 50% sulfuric acid. Together, these extractions served as a cleanup procedure, removing neutral and acidic oil components into the organic solvent and leaving bases in the aqueous phase. In the case of oil or octanol samples, an extraction of the oil with 0.1 N sulfuric acid was made in the presence of 25 mL methylene chloride. The acid extract pulled bases from the organic phase into aqueous solution. This solvent extract served as a wash and was repeated one time. To ensure adequate analytical recoveries of all basic components, an acidic back extraction of the combined methylene chloride washes was performed and the resulting aqueous phase was combined with the original aqueous sample. The pH of this combined aqueous sample was adjusted to 12 with 50% sodium hydroxide and extracted two times with methylene chloride. These organic extracts, containing the basic primary amines and nitrogen heterocyclic bases, free from most neutral and acidic components, were combined, and the solvent was exchanged for heptane. Solvent exchange was accomplished through evaporation of the methylene chloride to 1.0 mL under a gentle stream of nitrogen without the use of external heat. One mL heptane was added to the sample, and the sample was re-evaporated to 1.0 mL. The addition of 1.0 mL heptane and reevaporation was repeated to ensure volatilization of all methylene chloride. This solvent exchange was essential because the use of a chlorinated solvent in the NPD temporarily modifies its sensitivity, making quantification difficult. Benzanilide was chosen as the internal standard for GC analysis because it elutes later than most components of interest and causes no interference yet is chemically similar.

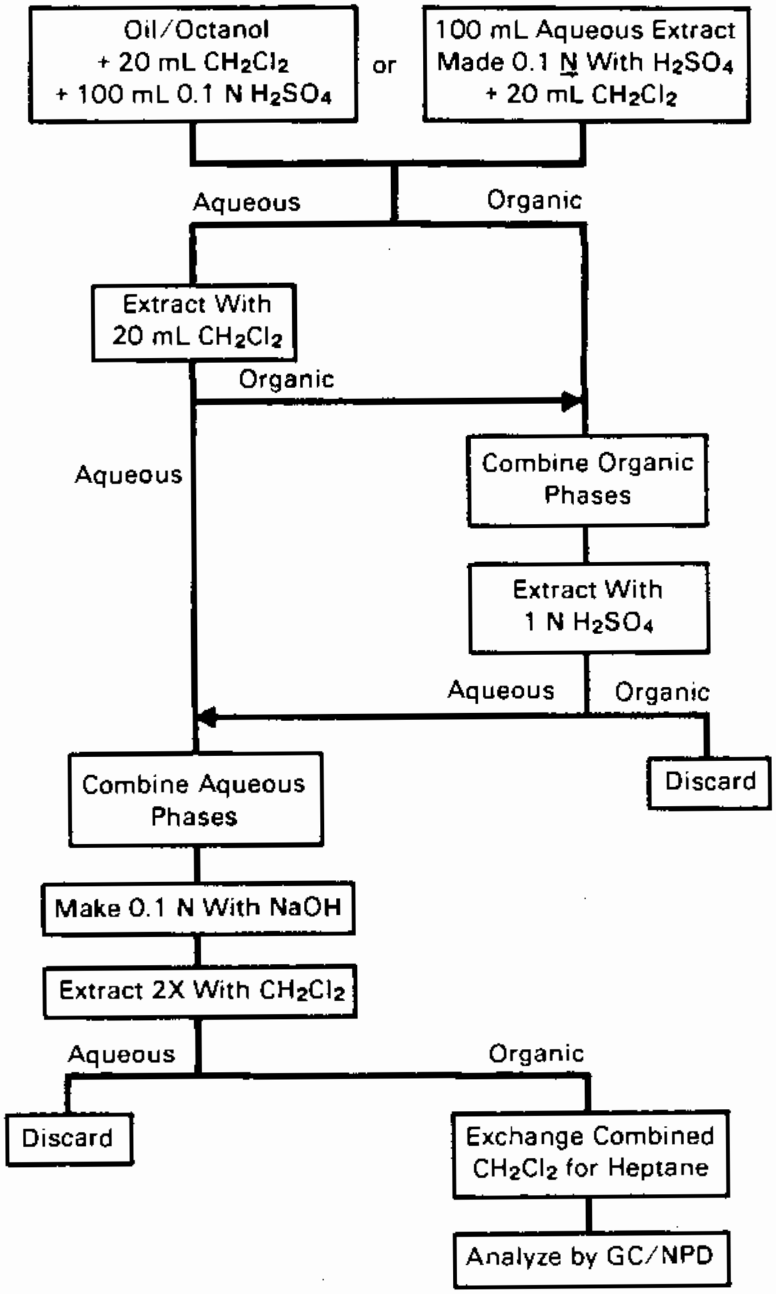

FIGURE 4. Flow Chart for Analysis of Nitrogen Bases

Figure 5 shows NPD and FID chromatograms of an SRC II WSF. Note that hydrocarbon interference peaks disappear in the NPD trace. Use of dual NPD and FID permits analysis of nitrogen components even in the presence of low levels of hydrocarbons. The FID shows not only the nitrogen bases of interest but also any organic contaminants that have come through the isolation scheme. Because hydrocarbons are present in relatively greater concentrations in the oils than are nitrogen bases, some of the hydrocarbon components remain with the basic oil fraction in spite of sample cleanup extractions.

Standard compounds representative of those measured in an oil WSF were subjected to extractions in triplicate, both from methylene chloride/octanol solutions and from aqueous solutions to simulate extraction of components of interest from oil/octanol or aqueous solution, respectively. Results show that recoveries using the aqueous or nonaqueous standard solutions are statistically identical. Recoveries are shown in Table 4. Percent recovery reported for each component is the averaged result of both sets of triplicate analyses. All calculated concentrations are corrected for these procedural losses.

Calibration factors for GC quantification were determined by injecting 2 μL of a mixture made up of known amounts of standard nitrogen bases to which had been added a known amount of benzanilide internal standard onto the GC columns and operating the GC with parameters used for sample analysis. Sensitivity of the NPD varies widely according to the operating voltage applied to the detector, which, in turn, affects the temperature and thus the volatilization rate of the alkali metal. As the collector ages, a higher voltage must be applied to maintain adequate sensitivity. Therefore, calibration standards were run frequently during sample analysis.

Anilines were differentiated from pyridines using the procedure of Felice (28). Aqueous anilines, because of their labile protons, are derivatized quickly at room temperature to form their respective acetanilides by the addition of a small amount of acetic anhydride. Figure 6 shows the total ion chromatogram and its associated single ion chromatogram of nitrogen bases isolated from a No. 2 fuel oil WSF. Figure 7 shows EPA/NIH spectra of a dimethylpyridine, aniline, and the spectrum of aniline present in an SRC II WSF, respectively. Figure 8 shows NPD chromatograms of a SRC II WSF both before and after derivatization. Acetylated anilines are easily recognized by comparing retention times of a nitrogen base mixture before and after derivatization. Note in Figure 8 that many of the earlier eluting peaks present in the unacetylated sample

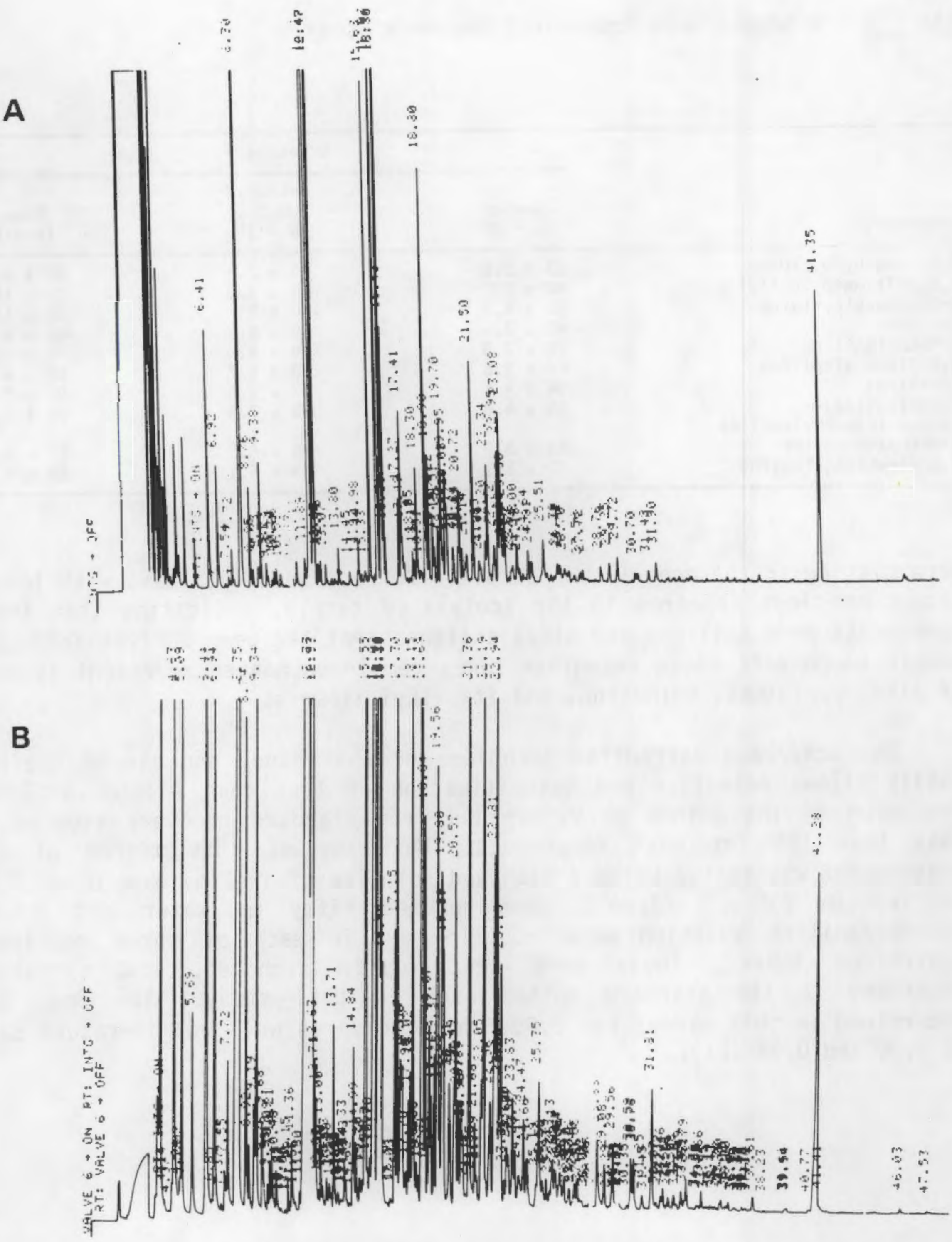

FIGURE 5. Gas Chromatograms from SRC-II WSF Nitrogen Base Fraction
(A) FID Detector (B) NPD Detector

TABLE 4. Nitrogen Base Procedural Recovery Study

Component	% Recovery		
	Aqueous (n = 3)	Octanol/ CH_2Cl_2 (n = 3)	Mean (n = 6)
2,5-Dimethylpyridine	53 ± 5.9	55 ± 7.4	54 ± 6.1
2,4,6-Trimethylpyridine	60 ± 20	82 ± 3.9	70 ± 18
p-Tertbutylpyridine	88 ± 4.7	100 ± 15	92 ± 11
Aniline	43 ± 3.4	46 ± 5.9	44 ± 4.6
2-Methylaniline	76 ± 2.8	78 ± 4.9	77 ± 3.8
2,4-Dimethylaniline	86 ± 3.6	89 ± 5.7	88 ± 4.4
Quinoline	94 ± 4.1	97 ± 6.6	96 ± 5.2
Isoquinoline + 2,4,6-Trimethylaniline	90 ± 4.8	93 ± 7.3	91 ± 5.8
8-Methylquinoline	85 ± 3.9	89 ± 6.5	87 ± 5.2
2,6-Dimethylquinoline	87 ± 4.3	89 ± 6.1	88 ± 4.9

were missing in the acetylated sample. Correspondingly, peaks with longer retention times appeared in the acetylated sample, indicating that these components were anilines and alkyl anilines that had been derivatized. The sample components whose retention times remain unchanged represent isomers of alkyl pyridines, quinoline, and its alkyl isomers.

The acid/base extraction technique of this study and use of the NPD easily allows detection and quantification of less than 1 μg/mL aniline. Precision of the method as determined from standard recovery studies is less than 10% for most components. Accuracy of this method of K_{ow} measurement was tested using a standard solution of aniline made up of 5 μL aniline in 2.0 mL octanol. One hundred fifty mL water and 0.5 mL octanol/aniline solution were equilibrated in each of three replicate centrifuge tubes. These were centrifuged, siphoned, and extracted according to the standard method used in this study. The $\log_{10} K_{ow}$ determined in this manner was 0.89, which compares well to literature data of 0.90 and 0.98 (21).

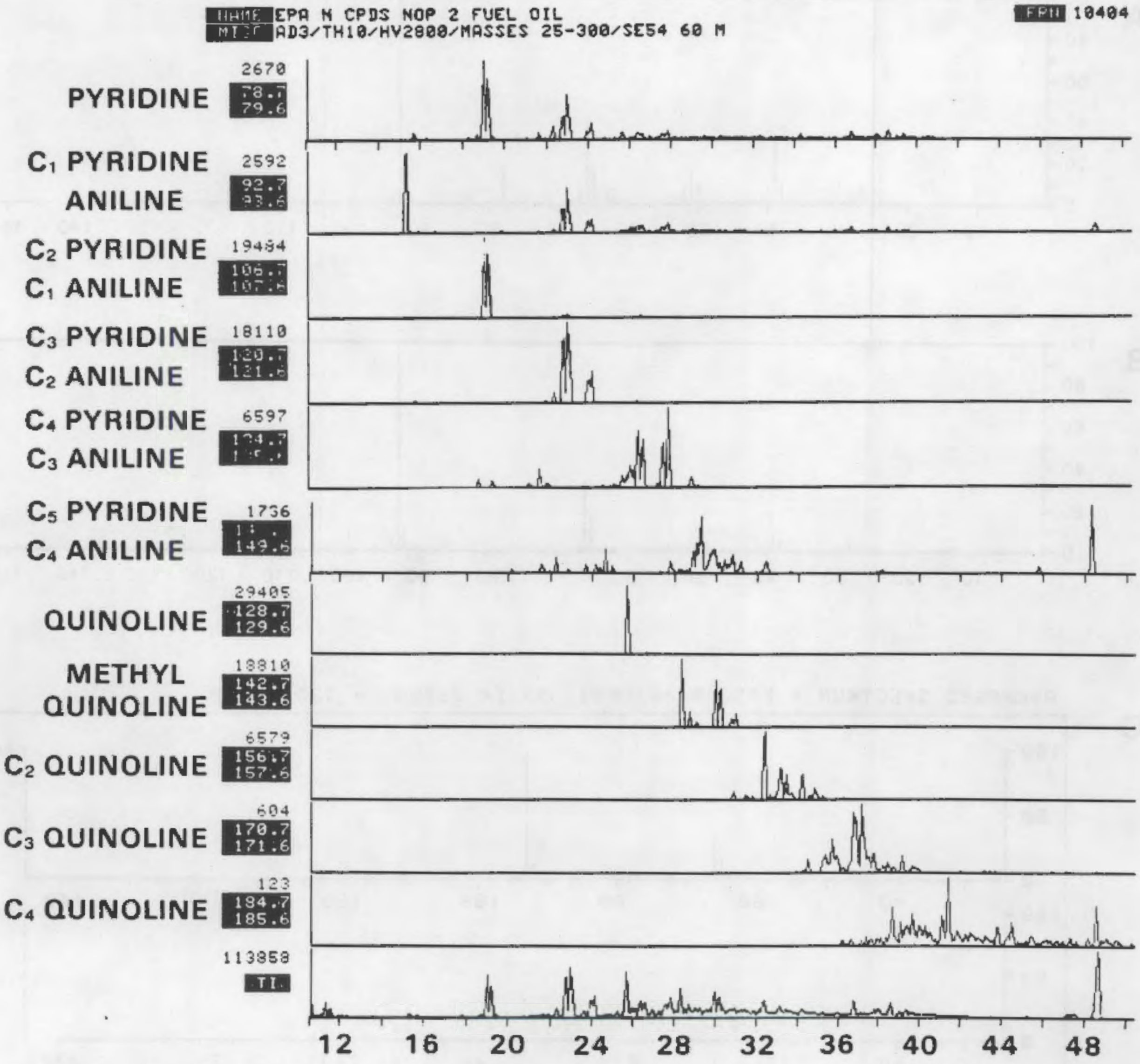

FIGURE 6. No. 2 Fuel Oil WSF Nitrogen Base Fraction Selected Ion and Total Ion Chromatograms

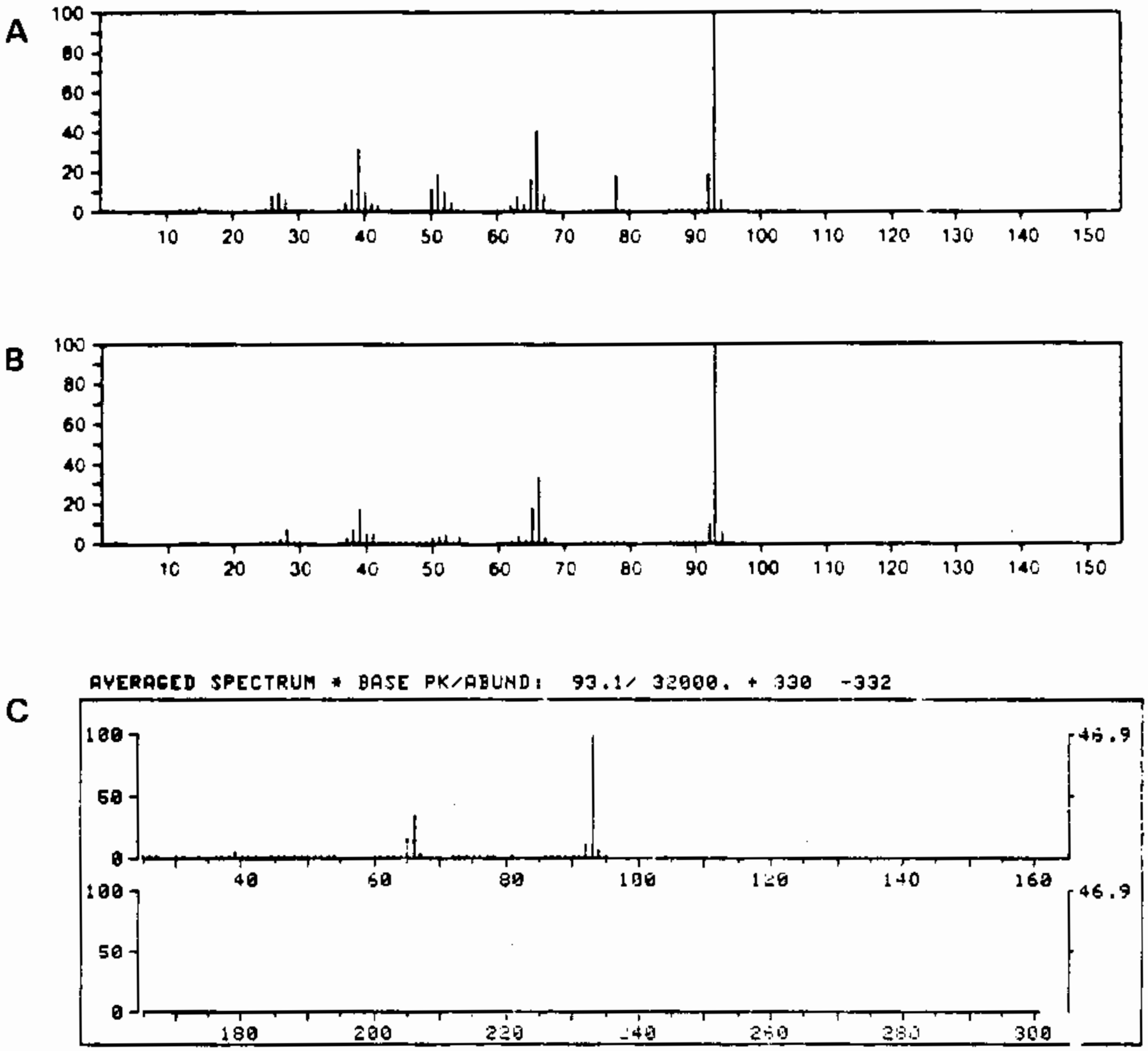

FIGURE 7. Nitrogen Base Mass Spectra
(A) EPA/NIH Spectrum of 2-Methyl Pyridine
(B) EPA/NIH Spectrum of Benzenamine (Aniline)
(C) Aniline Spectrum from SRC II WSF

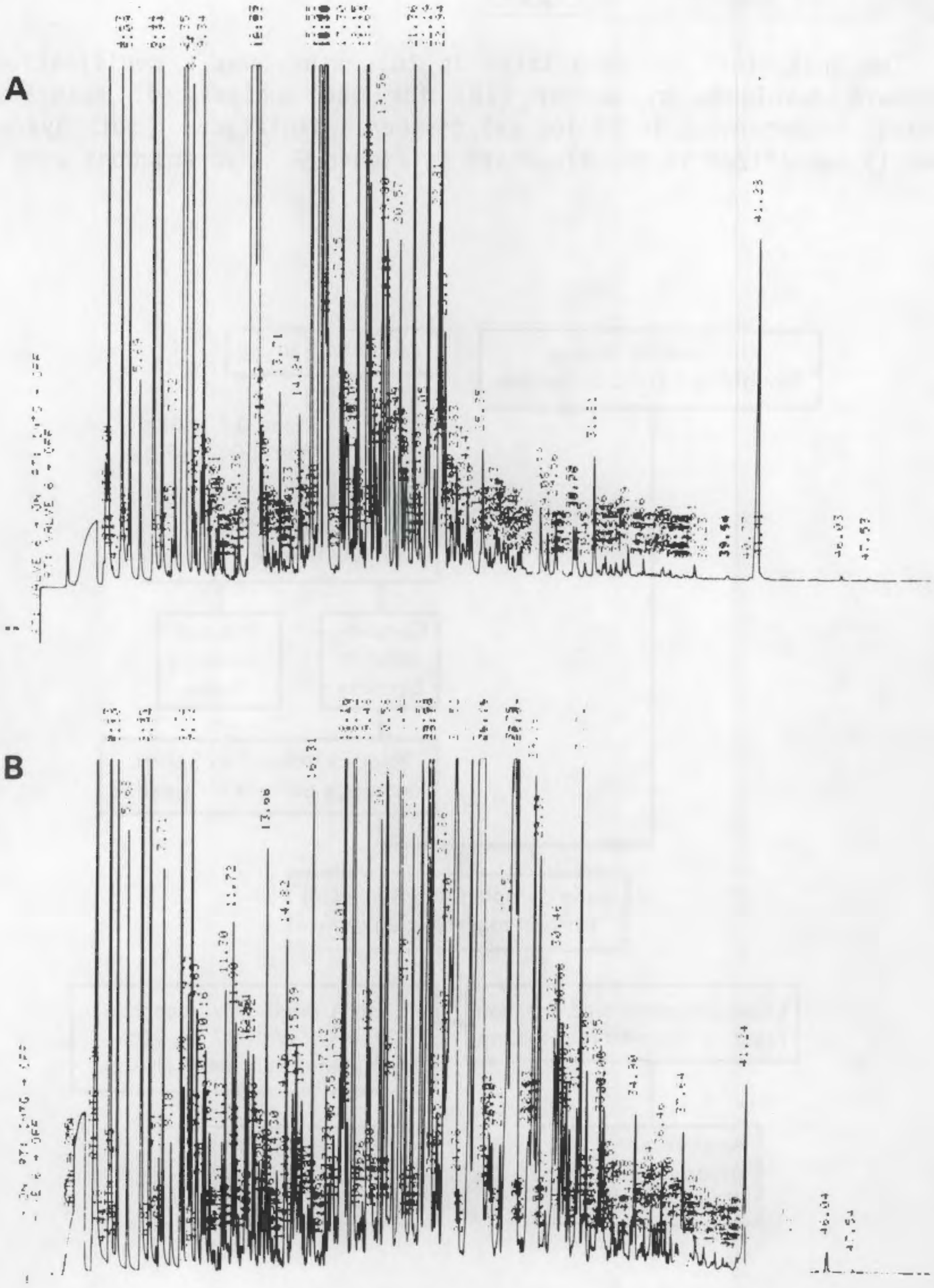

FIGURE 8. Gas Chromatograms of SRC II WSF Nitrogen Bases
(A) Unacetylated (B) Acetylated

SATURATED AND AROMATIC HYDROCARBONS

The analytical approach taken in this study was a modification of a procedure developed by Warner (78) for the analysis of saturated and aromatic hydrocarbons in biological tissues. Isolation of both hydrocarbon types is summarized in the flowchart in Figure 9. Hydrocarbons were

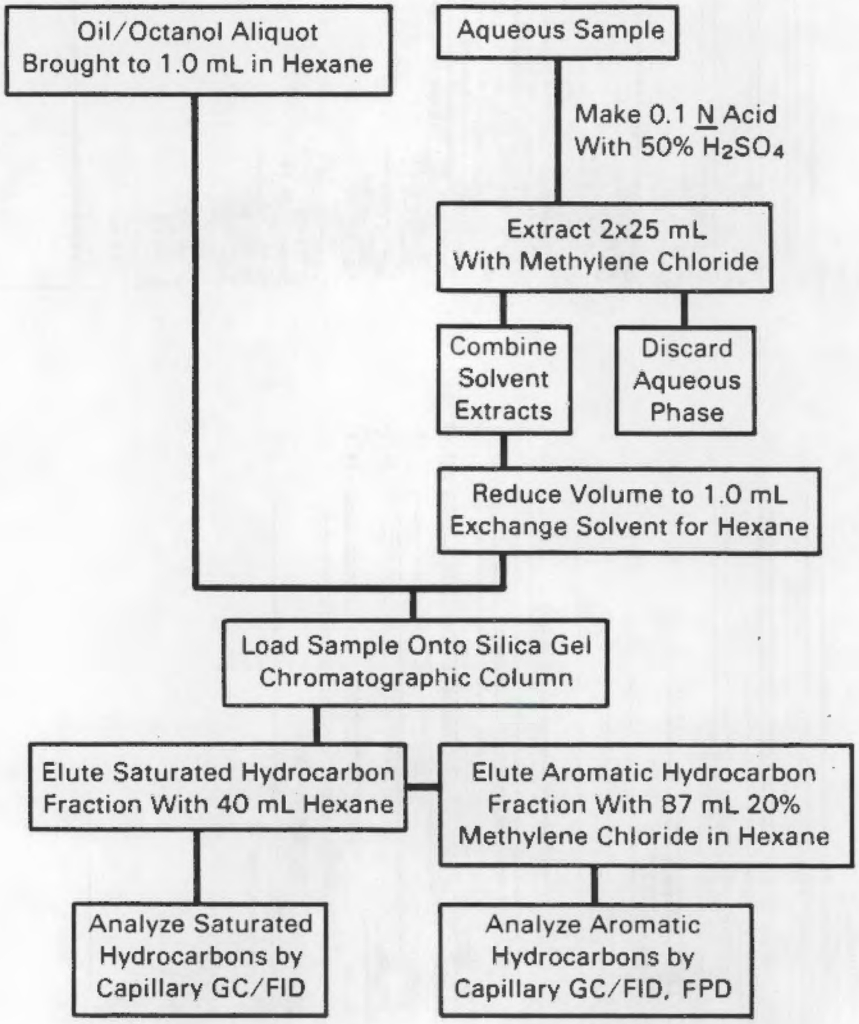

FIGURE 9. Flow Chart for Analysis of Hydrocarbons and Sulfur-Containing Heterocyclic Compounds

extracted from aqueous phases after addition of 0.5 mL 50% sulfuric acid to render the pH of the solution less than 1. Extraction was accomplished by two 25 mL methylene chloride extracts that were subsequently combined and reduced in volume to 1 mL under a stream of nitrogen using no external heat. The methylene chloride solvent was exchanged for hexane. Methylene chloride extracts contained neutral hydrocarbons and acidic contaminants. Isolation of aromatic and saturated hydrocarbon fractions from contaminants was accomplished through silica gel chromatography. Oil samples (10 mg) were dissolved in hexane for silica gel separation. Octanol samples required no preparation prior to silica gel chromatography.

Fifteen grams of activated Davidson 100/200 mesh silica gel were hexane slurry packed into Chromoflex® chromatographic columns. Any interfering organic contaminants present on the silica gel were removed by passing 30 mL methylene chloride through the column and discarding this wash. All methylene chloride was removed from the column by washing with 40 mL hexane. The sample was then loaded onto the top of the column. Saturated hydrocarbons were eluted with 40 mL hexane. Aromatic hydrocarbons were subsequently eluted with 87 mL 20% methylene chloride in hexane. Polar contaminants remained on the head of the silica gel column. Both saturated and aromatic hydrocarbon fractions were concentrated under nitrogen to a solvent volume of 1 mL. One mL of an appropriate internal standard was added. Hexamethylbenzene was chosen as internal standard for analysis of aromatic components and 2,6,10-trimethyldodecane was used as the saturated hydrocarbon internal standard. Samples were shaken thoroughly and aqueous phase samples following octanol equilibration were further evaporated to less than 250 µL for GC analysis because concentrations were very low and this additional concentration step was necessary for hydrocarbon detection and quantification. Oil phases and octanol phases were analyzed at a final volume of 2 mL. Quantification of both aliphatic and aromatic hydrocarbons was done using FID.

Saturated, straight chain hydrocarbons are easily identified by congruency of retention times with analytical standards because they elute as a homologous series. Aromatic hydrocarbons were also identified by comparison of GC retention times of sample components with analytical standards. A GC/MS analysis of an SRC II WSF confirmed the identity of aromatic components. Figure 10 shows the spectra obtained for naphthalene and a methyl-substituted naphthalene in a WSF extraction of SRC II. Other components' identities were similarily confirmed. Aromatic hydrocarbons yield a strong molecular ion in their mass spectra, so are identified relatively easily according to skeletal ring structure and degree of aliphatic substitution. However, positional isomers are not easily

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** Spectrum # 12 **   Sample #       1   Retention Time =18.58 minutes
Scanned from  50 to 300 amu  Number of Peaks Detected =   52
File type = linear
Base Peak = 127.90  Base Peak Abundance =      406  Total Abundance =      988
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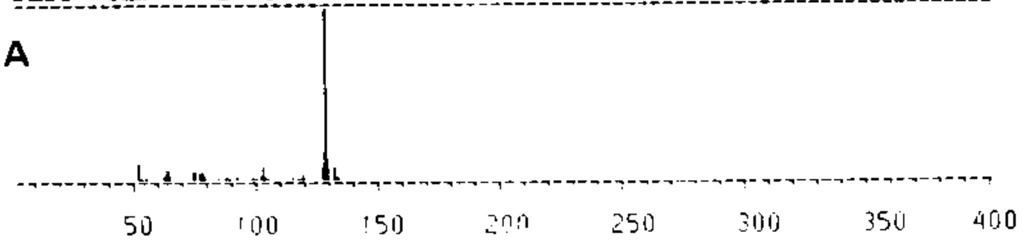

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Lower Abundance Cutoff Level =    2.0%
 MASS      ABUNDANCE (%)          MASS     ABUNDANCE (%)          MASS    ABUNDANCE (%)
 50.95         10.1               76.95        4.7               126.00       8.1
 51.85          3.0               78.00        3.0               127.00      15.8
 62.95          6.2              100.90        2.7               127.90     100.0
 [illegible]    5.7              102.00        8.4               128.90      12.3
 [illegible]    4.7              103.00        2.2               130.90       8.1
 [illegible]    5.2              119.00        3.4               133.00       2.5
 75.85          3.9
```

```
** Spectrum # 21 **   Sample #       1   Retention Time =22.58 minutes
Scanned from  50 to 300 amu  Number of Peaks Detected =   69
File type = linear
Base Peak = 142.00  Base Peak Abundance =      265  Total Abundance =     1067
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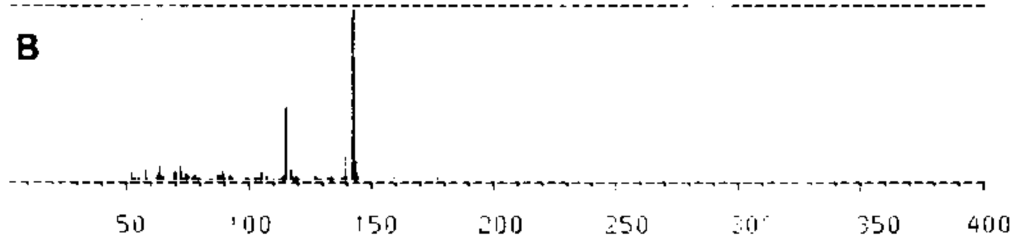

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Lower Abundance Cutoff Level =    2.0%
 MASS      ABUNDANCE (%)          MASS     ABUNDANCE (%)          MASS    ABUNDANCE (%)
 50.95          5.3               74.95        3.4               112.90       3.0
 57.35          6.0               76.95        2.6               114.90      41.5
 61.95          4.2               85.90        2.6               116.00       5.7
 62.85          9.4               86.90        2.6               118.90       2.3
   [illegible]  2.3               87.90        3.0               126.00       3.0
 [illegible]    4.5               89.00        5.7               138.90      12.8
 [illegible]    4.9               90.90        2.6               141.00      94.3
 70.85          3.7               92.00        2.3               142.00     100.0
 [illegible]    4.2              104.90        5.3               143.00      10.6
```

FIGURE 10. Aromatic Hydrocarbon Spectra from SRC II WSF (A) Naphthalene Spectrum (B) Methylnaphthalene Spectrum

differentiated by their mass spectra, and therefore identification relied upon retention time studies using analytical standards.

Recovery studies of both saturated and aromatic hydrocarbons were conducted simulating both aqueous and oil/octanol samples and are summarized in Tables 5 and 6. Known quantities of standard mixtures of both aromatic and saturated hydrocarbons were amended to water contained in a separatory funnel. Aqueous recovery standards were subjected to the extraction and analysis procedure detailed above. Recovery of aromatic

TABLE 5. Saturated Hydrocarbon Procedural Recovery Study

	% Recovery (n = 3)	
Component	Hexane Solution Silica Gel	Solvent Extract of Aqueous Sample Followed by Silica Gel
C_8	66 ± 2.2	57 ± 4.7
C_9	83 ± 2.5	44 ± 2.5
C_{10}	89 ± 2.1	53 ± 2.7
C_{11}	91 ± 1.4	60 ± 2.5
C_{12}	92 ± 1.0	64 ± 2.0
C_{13}	93 ± 1.1	69 ± 1.1
C_{14}	94 ± 1.6	73 ± 0.4
C_{15}	90 ± 2.3	78 ± 0.2
C_{16}	89 ± 2.6	81 ± 0.3
C_{17}	87 ± 2.8	84 ± 0.6
C_{18}	90 ± 2.0	89 ± 0.7
C_{19}	99 ± 2.1	92 ± 0.8
C_{20}	95 ± 3.0	95 ± 0.7
C_{21}	98 ± 3.7	96 ± 0.7
C_{22}	93 ± 1.2	96 ± 0.8
C_{23}	97 ± 1.6	96 ± 1.0
C_{24}	96 ± 2.3	100 ± 1.3
C_{25}	91 ± 0.5	106 ± 2.3
C_{26}	88 ± 1.2	110 ± 2.1

TABLE 6. Aromatic Hydrocarbon Procedural Recovery Study

	% Recovery (n = 3)		
Component	Hexane Solution Silica Gel	Solvent Extract of Aqueous Standards Followed by Silica Gel	Solvent Extract of Aqueous Standards Followed by Silica Gel and Volume Reduction
Ethylbenzene	50 ± 4.8	34 ± 3.6	16 ± 2.1
m+p-Xylene	56 ± 4.7	39 ± 3.7	27 ± 3.3
o-Xylene	59 ± 4.3	42 ± 3.8	31 ± 2.6
Isopropylbenzene	67 ± 3.7	49 ± 4.0	16 ± 3.6
1-Ethyl-4-methylbenzene	73 ± 3.1	56 ± 4.1	28 ± 3.7
1,2,4-Trimethylbenzene	77 ± 2.7	58 ± 4.2	32 ± 4.2
Secondary butylbenzene	79 ± 2.9	59 ± 4.3	15 ± 4.7
1-Methyl-4-isopropylbenzene	80 ± 2.5	61 ± 4.2	19 ± 4.5
1,3-Dimethyl-5-ethylbenzene	82 ± 2.4	66 ± 3.3	22 ± 4.9
1,2-Diethylbenzene	82 ± 2.5	62 ± 2.2	24 ± 4.5
1,2-Dimethyl-4-ethylbenzene	82 ± 2.8	64 ± 4.0	26 ± 4.4
1,2,3,5-Tetramethylbenzene	84 ± 2.3	67 ± 3.6	32 ± 4.3
Naphthalene	84 ± 2.5	67 ± 3.4	59 ± 0.7
Benzothiophene	76 ± 1.8	55 ± 1.5	56 ± 2.4
2-Methylnaphthalene	85 ± 2.3	71 ± 2.5	60 ± 2.1
1-Methylnaphthalene	85 ± 2.3	73 ± 2.3	61 ± 2.0
Biphenyl	84 ± 2.0	75 ± 1.8	65 ± 0.9
2,6-Dimethylnaphthalene	86 ± 1.6	76 ± 1.7	58 ± 3.0
2,3,5-Trimethylnaphthalene	86 ± 1.8	83 ± 1.2	64 ± 2.8
Fluorene	86 ± 1.0	85 ± 1.7	76 ± 1.9
Dibenzothiophene	52 ± 3.8	30 ± 4.9	60 ± 21
Phenanthrene	91 ± 3.0	92 ± 1.4	76 ± 1.1
Anthracene	92 ± 1.5	93 ± 2.1	83 ± 5.0
1-Methylphenanthrene	95 ± 2.4	84 ± 1.8	81 ± 1.3
Fluoranthene	92 ± 3.4	101 ± 2.8	85 ± 2.8
Pyrene	87 ± 3.2	100 ± 2.6	85 ± 1.3

standard compounds at dilute concentrations, approaching those found in aqueous phases resulting from equilibration of an oil WSF with octanol, was determined by following the methylene chloride extraction procedure and silica gel separation with concentration of the sample to 200 µL before GC analysis. Recovery of standard compounds at low concentrations with this evaporation step gave low recoveries, ranging from 16% for some of the alkyl-substituted benzenes to 85% for fluoranthene. Standard deviations associated with recoveries of the low concentration aqueous standards were higher than those associated with higher concentration aqueous standard solutions. Recovery from oil/octanol was determined by subjecting a hexane solution of standard hydrocarbons to silica gel separation and subsequent analysis.

Naphthalene was chosen as a representative 2-ring aromatic hydrocarbon to test the ability of this method to generate K_{ow} data comparable to that in the literature, yielding a log K_{ow} of 3.14 ± 0.05 for a triplicate experiment that compares very well with literature K_{ow} of 3.37, 3.01, and 3.45 (21). Ortho-xylene was partitioned between octanol and water to test the method for single-ring aromatic compounds. Aqueous phase concentrations were highly variable, yielding K_{ow} data that differed by a factor of 10 between replicate measurements. The hydrophobic, volatile, single-ring aromatic hydrocarbons were very difficult to quantitate accurately in aqueous phases, generally giving log K_{ow} values larger than literature values because apparent aqueous concentrations were lower than those predicted from literature K_{ow} data. Low aqueous phase concentration could be explained by volatilization of low molecular weight components during siphoning or adsorption of these components on the inside surface of the Teflon® tubing used for siphoning aqueous phases from the glass container used for equilibrating an oil WSF with octanol.

HETEROCYCLIC SULFUR COMPOUNDS

The analytical approach taken in this study utilized silica gel chromatography and gas chromatography using FID and FPD. Sulfur-containing heterocyclic components are isolated along with the aromatic hydrocarbon fraction from silica gel chromatography (Figure 9). Analysis of aromatic hydrocarbon fractions that had been further reduced in volume was performed using GC/FID. Flame photometric chromatographic results showed sulfur species were present in each of the four oils analyzed. However, concentrations, for the most part, were quite low. The aromatic hydrocarbon standard mix used in this study contained both benzothiophene and dibenzothiophene; consequently, FID response factors were applied to yield concentrations of these two components. The retention times of benzothiophene and dibenzothiophene analytical standards corresponded to FPD chromatographic peaks; as a result, use of the FPD served to confirm the identification by retention time of these components. No quantification was done using FPD, however. Concentrations of sulfur species other than benzothiophene and dibenzothiophene were determined to be too low to accurately quantify. Other sulfur heterocyclic components present in samples most likely were alkyl substituted benzothiophenes and dibenzothiophenes. The use of larger initial oil samples (79) would permit quantification of these components. However, the analytical scheme used in this study limits the size of initial oil samples so that the silica gel in the oil fractionization procedure is not overloaded. Aqueous phase samples are also necessarily limited in volume. Redesign of the analytical scheme for sulfur heterocyclic components could provide a challenging project for follow on work but was determined to be beyond the scope of this study.

Procedural recovery of benzothiophene and dibenzothiophene was determined in the experiment to determine recoveries of aromatic hydrocarbons (Table 6). The recoveries of both sulfur components were found to be somewhat lower and more variable than those of the aromatic hydrocarbons.

CARBOXYLIC ACIDS

The isolation procedure used in this study is illustrated in Figure 11. Acids in aqueous solution were extracted with 25 mL methylene chloride after acidification of the aqueous phase to pH 1 with 50% sulfuric acid. The solvent extraction was repeated once and extracts were combined. Acidification of the initial aqueous sample caused only acids and neutral components to be solvent extracted, leaving basic components in the aqueous phase. Acids were subsequently extracted from methylene chloride into 0.1 N sodium hydroxide, leaving neutral components in the organic phase. Acids present in the oil or octanol samples were extracted into 0.1 N sodium hydroxide. The hydroxide solution, containing acid sodium salts, was acidified by addition of 50% sulfuric acid and extracted two times with 25 mL methylene chloride. Both phenols and carboxylic acids are acidic and were present in methylene chloride extracts, so that further cleanup of the samples was necessary. Two 5-mL sodium bicarbonate extracts of the methylene chloride isolated a relatively pure aqueous carboxylic acid fraction because dissociation constants of phenols are higher than acids. Phenols remained, therefore, in the organic phase.

Free acids were derivatized by boron trifluoride in methanol to their methyl esters. Because this derivatization procedure must be done in a medium free from water which destroys the boron trifluoride acid catalyst, the sodium bicarbonate extracts were freeze-dried before reaction with 2-mL boron trifluoride in methanol at 80°C for 1 hour. Upon cooling to room temperature, methanol solutions of methyl esters were transferred to 60-mL separatory funnels using 5 mL hexane. Ten mL saturated aqueous sodium chloride solution was added to each separatory funnel. The aqueous sodium chloride served to destroy any residual boron trifluoride and also to partition the methanol away from hexane-soluble methyl esters. Hexane phases were isolated and hexamethylbenzene internal standard was added to the samples. Methyl ester samples were qualitatively analyzed using GC/MS and were quantified by GC/FID.

Flame ionization responses for individual acid components were determined by subjecting a methanol solution of analytical standards, including both aliphatic and aromatic carboxylic acids, to the procedure

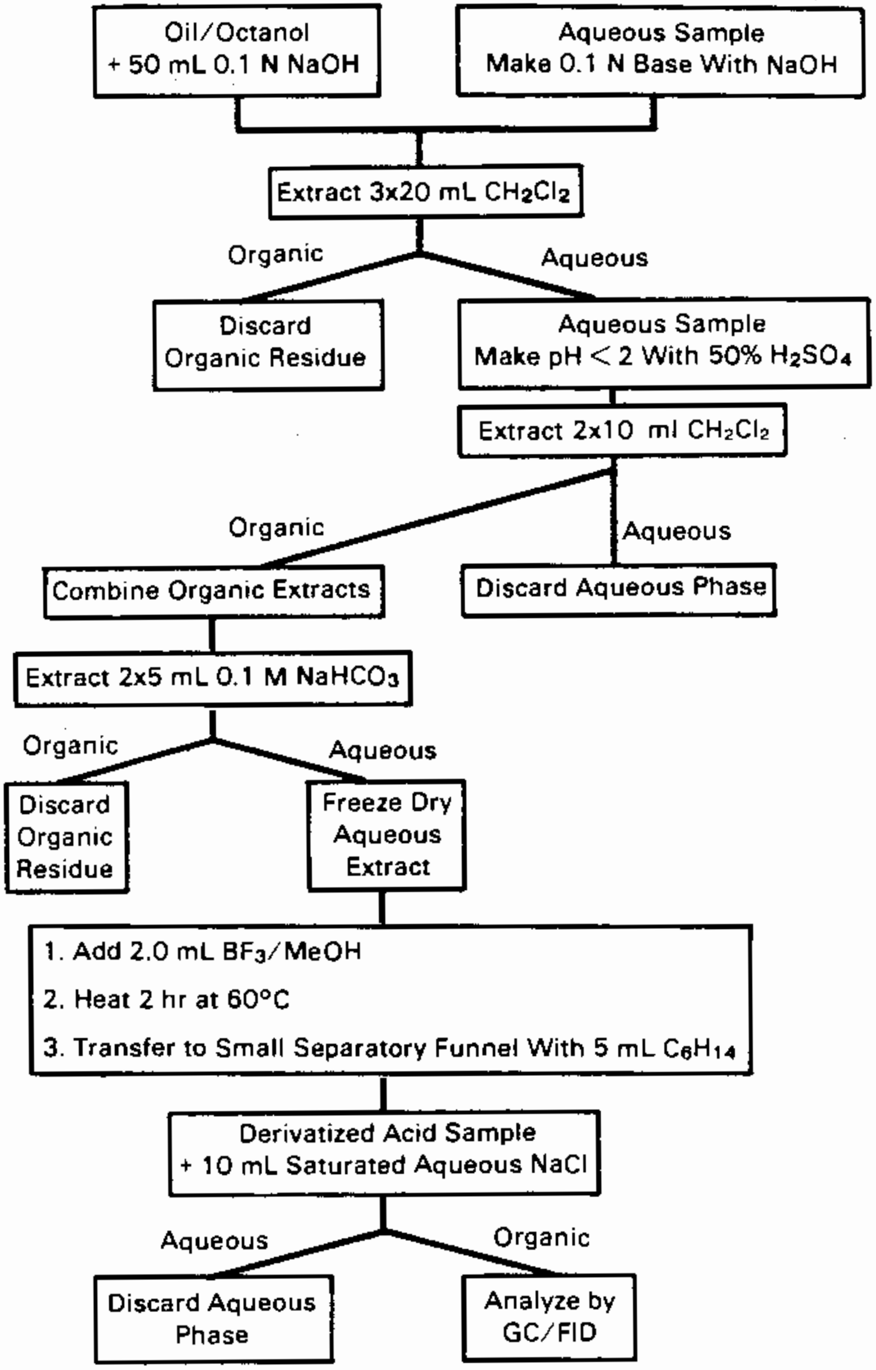

FIGURE 11. Flow Chart for Analysis of Carboxylic Acids

detailed above. Acid standards were recovered both from aqueous solution and from a hexane solution (to simulate recovery from oil or octanol samples). Calibration factors were calculated for aqueous and nonaqueous acids and differences were judged negligible. Calibration factors derived in this fashion provided the relative response of the FID to each component and also corrected results for procedural losses.

Precision of the method was determined to be 10%. Aqueous acid concentrations lower than 10 µg/L could be determined easily in a 100-mL aqueous sample. Procedural blanks of both aqueous and octanol phases were analyzed and showed that, while there were some small extraneous peaks, none interfered with analysis of the acids of interest.

Procedural recovery of octanoic acid was determined by subjecting a methanol solution of octanoic acid to the analytical scheme and calculating the amount of acid recovered, using a calibration factor determined for methyl octanoate in hexane. Recovery of octanoic acid was 80.6%.

The ability of the method to generate accurate K_{ow} data was examined by dissolving hexanoic acid in octanol and subjecting an aliquot of this octanol solution to equilibration with distilled water. Both octanol and aqueous phases were quantitated. The log K_{ow} for hexanoic acid was 1.70, which compares well with literature data of 1.88 and 1.92 (21). Hexanoic acid was chosen for this experiment because literature data is unavailable for carboxylic acids containing longer alkyl carbon chains.

Use of this analytical scheme was very effective for determination of monobasic acids with alkyl skeletons of six or more carbon atoms and for aromatic acids. It did, however, have the disadvantage of failing to recover dibasic acids, which are known to exist in oil-shale retort waters (38). Dibasic acids were lost in the aqueous sodium bicarbonate extraction that was designed to remove phenols. Perhaps in future studies derivatization of the acids using diazomethane could overcome this problem by making a sodium bicarbonate extraction unnecessary. Phenols might remain underivatized and cause no interference.

The method also lacks the ability to isolate and quantify aliphatic acids containing fewer than six alkyl carbons. These more volatile acids have been quantified through formation of less volatile butyl esters by substitution of butanol for methanol in the boron trifluoride/alcohol derivatization reaction (37), but attempts to utilize boron trifluoride in butanol as the esterification reagent were unsuccessful in this study. Butanol is considerably more lipophilic than methanol and must be separated from the resultant butyl ester/hexane solution by partition into an acetonitrile/water mixture. Attempts to free the samples of residual butanol prior to GC analysis met with variable success. Butanol is fairly volatile and traces remaining in the derivitized acid sample were eluted from a nonpolar GC column with the hexane solvent. The presence of any residual butanol caused severe tailing of the solvent and general degradation of the chromatographic separation. In addition to this obvious disadvantage of derivatization with butanol, blanks were judged to contain too many extraneous peaks for good chromatographic analysis.

Electron impact mass spectral analysis of aliphatic methyl esters showed the presence of characteristic mass peaks in each aliphatic methyl ester's spectrum corresponding to 59, 74, and 87 amu. The presence of these peaks in a spectrum indicates the presence of an aliphatic methyl ester. However, determination of its exact molecular weight and structure is difficult, because the molecular ion, if present at all, is very weak. Gas chromatographic retention time comparisons with standard methyl esters were used to determine how many carbon atoms a particular methyl ester contained. Figure 12 shows the spectrum for methyl octanoate found in a derivatized Oxy WSF and methyl octanoate from the EPA/NIH spectrum library.

Mass spectral analysis of benzoic acid-methyl ester yields the presence of a large ion at 77, base peak at 105, and the molecular ion at 136. The base peak for methyl substituted benzoic acid-methyl esters are 105 + 14. Figure 13 shows the benzoic acid-methyl ester from a SRC II WSF as well as the standard component EPA/NIH library spectrum.

INSTRUMENTATION AND REAGENTS

Gas chromatographic separation of samples in this study was accomplished on several different instruments using different columns, detectors, and different chromatographic parameters.

Phenol samples were analyzed with a Hewlett-Packard 5840A model gas chromatograph operated in the split mode with a 10:1 split ratio. The chromatographic column used for these analyses was a 60-m SP2100 fused silica capillary column manufactured by J and W Scientific Co., and detection was by FID. Chromatographic conditions were:

Initial temperature	65°C
Initial time	4 minutes
Program rate	4°C/minute
Final temperature	260°C
Final time	20 minutes

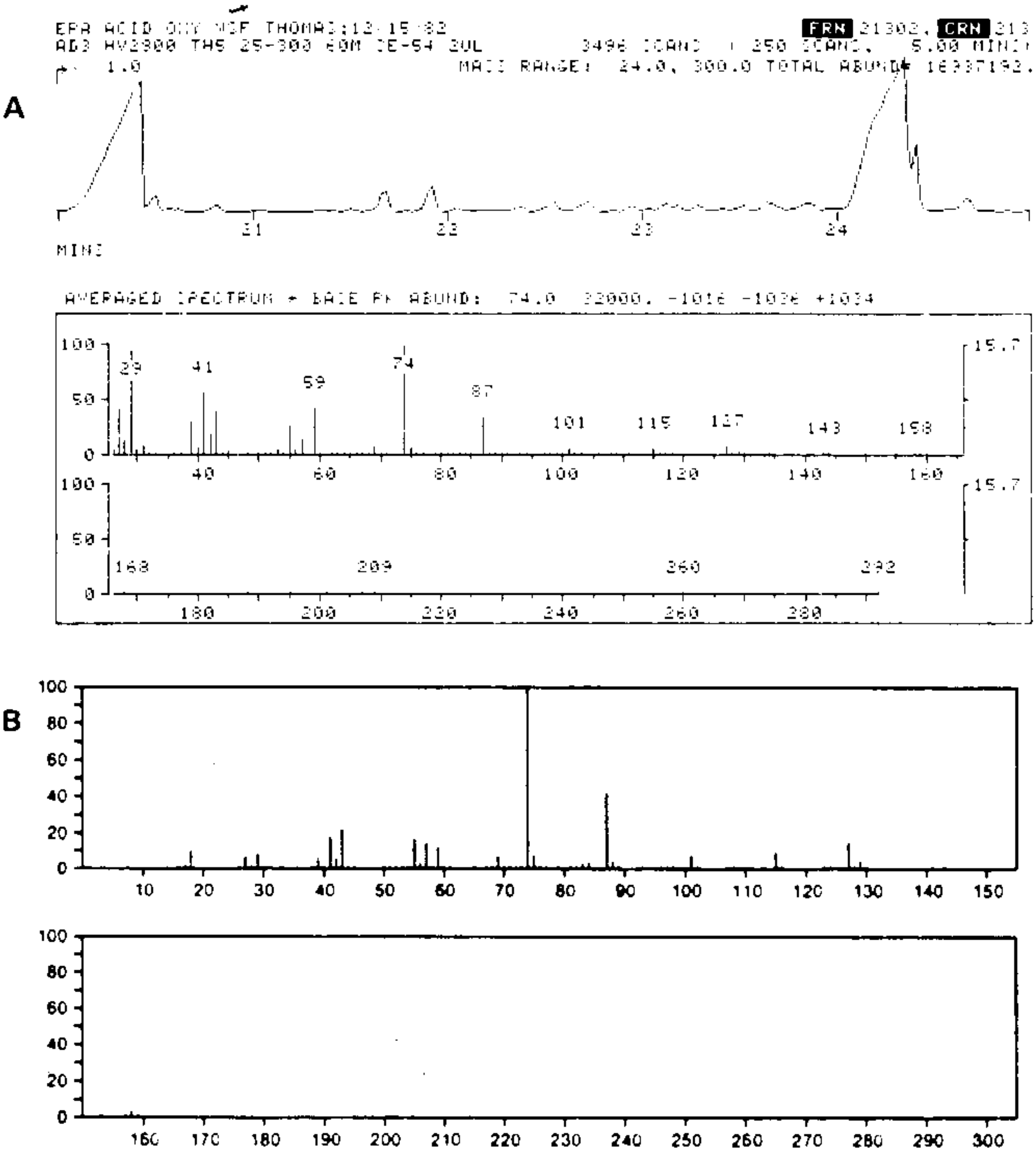

FIGURE 12. Aliphatic Acid - Methyl Ester Spectra
(A) Methyl Octanoate from Oxy WSF (B) EPA/NIH Methyl Octanoate

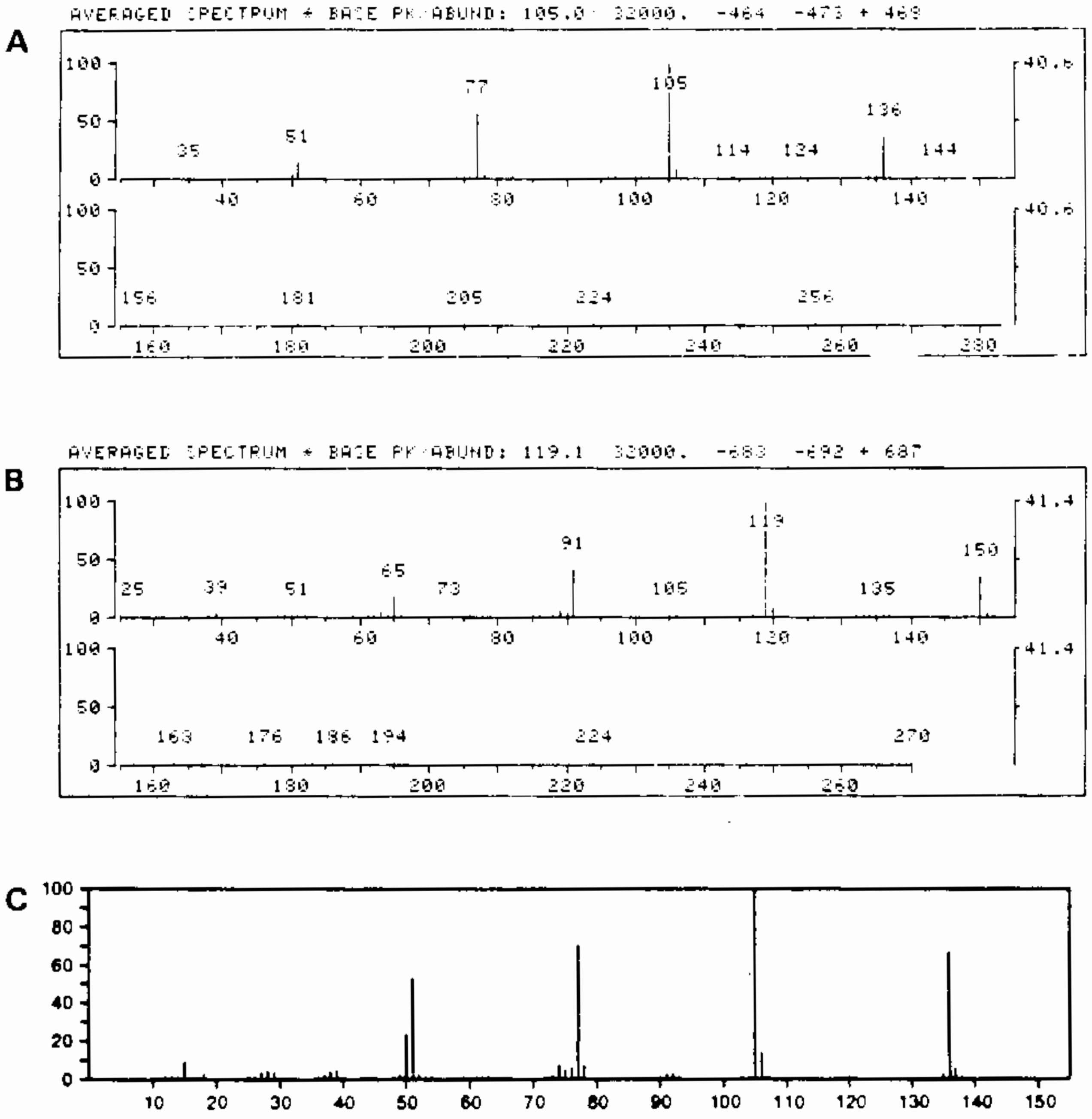

FIGURE 13. Aromatic Acid - Methyl Ester Spectra
(A) Benzoic Acid - Methyl Ester from SRC II WSF
(B) C_1 Benzoic Acid - Methyl Ester from SRC II WSF
(C) EPA/NIH Benzoic Acid - Methyl Ester

Nitrogen bases were analyzed with a Hewlett-Packard 5880A gas chromatograph operated in the splitless mode. This instrument was equipped with both FID and NPD. The sample was introduced into two matched J and W Scientific Co. 30-m fused silica SE54 capillary columns attached to a conventional injection port by a 2-hole graphite ferrule. Effluent from one column was monitored by NPD. The other column effluent was monitored by FID. Chromatographic conditions were:

Initial temperature	70°C
Initial time	4 minutes
Program rate	4°C/minute
Final temperature	260°C
Final time	20 minutes

Hydrocarbons and carboxylic acids were analyzed with the Hewlett-Packard 5840A chromatograph used to analyze phenols. The chromatographic column used was a 60-m DB5 fused silica capillary column manufactured by J and W Scientific Co. Detection was by FID. Chromatographic conditions were those used for phenol analysis.

Sulfur heterocyclic aromatic compounds were analyzed with the HP 5840A chromatograph used to analyze phenols and hydrocarbons. The chromatographic column was the DB5 capillary column used for hydrocarbons. Chromatographic conditions were the same as for hydrocarbons; however, detection was by a flame photometric detector (FPD) with a sulfur specific filter and by FID.

All solvents used were Burdick and Jackson distilled in glass spectrographic grade. Phenol analytical standards were purchased from Supelco, Inc. Nitrogen base standards were purchased from Pfaltz and Bauer, Inc. and from Aldrich Chemical Co., Inc. Aromatic carboxylic acid standards were purchased from Aldrich Chemical Co., and aliphatic carboxylic acids were purchased from Supelco. Benzothiophene and dibenzothiophene were purchased from Aldrich Chemical Co. Saturated and aromatic hydrocarbon analytical standards were purchased from Chemical Samples Co., Alltech Associates, and Aldrich Chemical Co. Acetic anhydride used for derivatization of phenols and anilines was obtained from Eastman Kodak Co. Prior to its use, it was distilled and stored in a desiccator. Boron trifluoride in methanol used for derivatization of carboxylic acids was purchased from Supelco. Davidson 100/200 mesh silica gel was used for isolation of hydrocarbons and sulfur heterocyclic compounds and was purchased from Supelco. Prior to its use, it was activated by heating in a 120°C drying oven overnight. It was subsequently stored in a desiccator.

Normal octanol used was Baker reagent grade purchased from VWR Scientific Inc. It was cleansed of contaminants following the EPA approved scheme (10) by washing it once with 0.1 N sodium hydroxide and two times with distilled water. It was then double distilled and stored in an amber glass bottle fitted with a Teflon®-lined screw cap.

Analysis by gas chromatography/mass spectrometry (GC/MS) was performed on WSF extractions using a Hewlett-Packard 5840A gas chromatograph operated in the splitless mode interfaced with a HP 5985 mass spectrometer operating in the electron impact mode and 7900/7920 multidisc drive systems. Masses scanned were from 25 to 400. All GC/MS separations were performed on a 60-m J and W Scientific DB5 fused silica capillary column, and chromatographic conditions were those used for GC analyses.

A derivatized SRC II WSF phenol sample was analyzed using a Hewlett-Packard 5970A mass selective detector (MSD) interfaced with a HP 5880 GC operated in the splitless mode. The chromatographic column used for this analysis was a 60-m J and W Scientific DB5 fused silica column. The MSD operates in the electron impact mode supplying 70 eV electrons for ionization. Chromatographic conditions were those used for GC analysis. Vendor-supplied software, Peakfinder, provided spectra for peaks eluted. Specific ions characteristic of acetylated phenol and alkyl phenols were monitored using a different vendor-supplied selected ion monitoring software program, SIM.

A Beckman model 915-B total organic carbon analyzer was used for the determination of organic carbon concentration in a WSF from each oil.

Distribution coefficients were determined mathematically from concentration data and expressed as mean ± standard deviation of three replicate samples through the use of a computer and a computer statistical package, MINITAB©, available from Pennsylvania State University. This software package allows the user to perform mathematical operations on columns of data, so that standard deviations of partition coefficients could be calculated quickly using the equation:

$$\frac{a \pm x}{b \pm y} = \frac{a}{b} \pm \frac{a}{b} {\left(\frac{x^2}{a^2} + \frac{y^2}{b^2} \right)}^{1/2}$$

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where a = mean oil/octanol concentration

x = 1 standard deviation of the oil/octanol concentration
b = mean aqueous concentration
y = 1 standard deviation of the aqueous phase concentration.

RESULTS AND DISCUSSION

The following section is organized by compound type. Component concentrations in oil, octanol, and aqueous phases are located in the appendix; tables of K_{ow} and K_{bw} are also shown. Correlations between K_{ow} and K_{bw} and degree of alkyl substitution (aromatic compounds) or carbon chain length (aliphatic acids) are shown graphically for each component type.

PHENOLS

Phenols were found to be present in each of the four oils examined in this study. Figure 14 shows gas chromatograms of the derivatized WSF phenol fractions for each oil type studied. Chromatographic patterns of phenol acetates of a WSF generated from each oil are similar, indicating most components are common to all oils. Table 7 shows total phenol concentrations in each of the oils and their associated WSF phenol concentrations in addition to TOC measured in each WSF. Aqueous phase TOC analyses measure not only water-solubilized phenols but also all other organic components that partition into the aqueous phase during equilibration of an oil with water. An SRC II WSF generated from a 100:1 water to oil equilibrium mixture contains much more organic carbon than does a WSF generated using an equivalent oil to water ratio from any of the other oils studied. Table 8 shows concentrations of individual phenols quantified in this study for each of the oils. SRC II was found to contain substantially greater amounts of phenolic material than the other oils studied; 26.6% of SRC II product oil can be accounted for as phenols. Oxy consists of 0.4% phenolic materials. No. 2 fuel oil contains only about 0.04% phenols, while PBC consists of about 0.01% phenols. This represents a range of more than four orders of magnitude from SRC II total phenol concentration. The concentration of unsubstituted phenol ranges from 2.47 µg/mL in PBC, to 6.76 µg/mL in No. 2 fuel oil, 144 µg/mL in Oxy, and a high of 35,000 µg/mL in SRC II. Concentrations of substituted phenols in the oils are not found in exactly those same proportions among the oils, but the trend from lowest concentrations in PBC to highest in SRC II is observed for all degrees of aliphatic substitution. A complete tabulation of selected phenol concentrations in all oil and aqueous phases for each oil is found in Tables 1A through 4A of the Appendix.

Table 9 shows the differences in log K_{bw} of phenol and its various alkyl substituted products among the oils studied. Averages were calculated for the various positional isomers having equivalent molecular

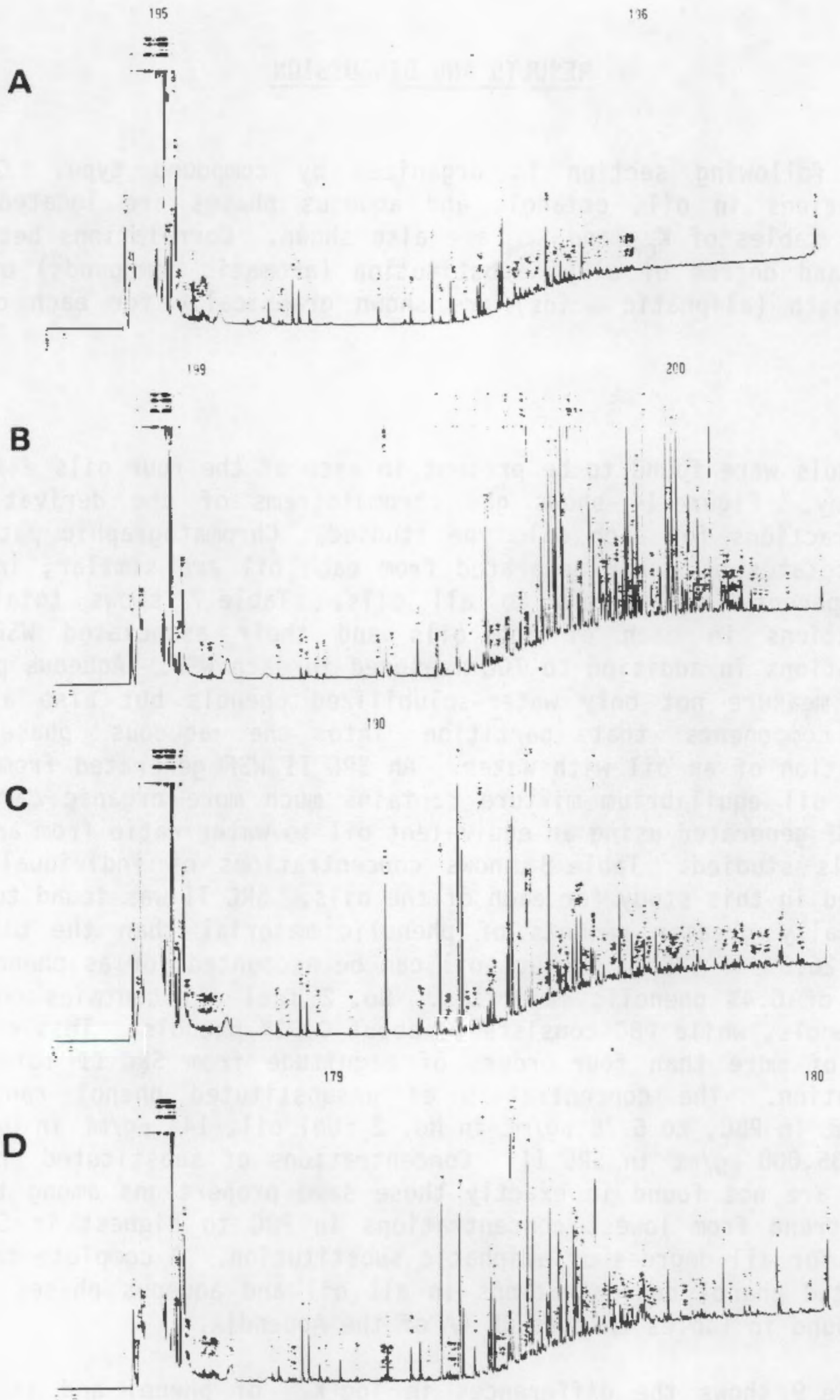

FIGURE 14. Gas Chromatograms of Derivatized WSF Phenol Fraction (A) PBC (B) SRC II (C) Oxy (D) No. 2 Fuel Oil

TABLE 7. Total Phenol Concentrations in Oils and Their Corresponding WSF (μg/mL)

Oil Type	Phenol Conc. in Oil	Phenol Conc. in WSF	TOC
SRC II	2,660,000 ± 12000	2,000 ± 40	10,800 ± 300
Oxy	3,950 ± 50	19.6 ± 0.3	89 ± 6
PBC	93 ± 1	0.7 ± 0.1	22 ± 3
No. 2 Fuel Oil	433 ± 7	4.1 ± 0.1	17 ± 1

weights. As might be expected, degree of alkyl substitution greatly affects K_{bw}; the more highly substituted components are much more lipophilic than unsubstituted phenol, tending to remain associated with water-insoluble oil components. In a given oil/water equilibrium mixture, phenols with equivalent alkyl substitution behave in a manner consistent with the degree of substitution, regardless of the position. This is illustrated by computing the mean log K_{bw} for different phenol isomers having equivalent alkyl substitution. For example, the mean and standard deviation log K_{bw} for C_3 phenols in SRC II is 2.32 ± 0.06. The small standard deviation shows that for a given oil, alkyl phenol isomers of equivalent molecular weight partition similarly between aqueous and oil phases. However, differences in K_{bw} are apparent between the oils studied. A linear least squares treatment of SRC II phenols yields the regression equation $Y = 0.97 + 0.40X$ with $R^2 = 84.4\%$, where X is the number of alkyl substituted carbon and Y is the log K_{bw}. Figure 15 shows log K_{bw} for SRC II phenols plotted against increasing alkyl substitution. Phenols with more than C_3 substitution have log K_{bw} that are much lower than those that would be predicted using the regression equation calculated from log K_{bw} for phenols with C_0 through C_3 alkyl substitution. Lower K_{bw} result from higher than expected measured C_4 and C_5 phenol concentrations in the aqueous phases following equilibration of the oils with water. These higher aqueous concentrations could be the result of formation of micelles, or aggregates, of the relatively nonpolar C_4 and C_5 phenols in the aqueous phases (49). Regression of No. 2 fuel oil log K_{bw} on degree of alkyl substitution for C_0 through C_5 gives the equation $Y = -0.150 + 0.540X$, with a slope similar to that obtained for SRC II phenol data but with a lower intercept. Oxy gives the equation $Y = 1.54 + 0.166X$ and PBC

TABLE 8. Phenol Concentrations in Oils

Component	RRT[1]	SRC II[2]	Oxy[3]	PBC[3]	No. 2 Fuel Oil[3]
Phenol	1.0000	350 ± 3	140 ± 2	2.5 ± 0.12	6.8 ± 0.20
o-Cresol	1.1754	160 ± 11	140 ± 1	6.2 ± 0.09	23 ± 0.7
m-Cresol	1.2319	410 ± 23	190 ± 1	2.1 ± 0.15	22 ± 0.2
p-Cresol	1.2446	230 ± 13	140 ± 1	2.7 ± 0.08	9.3 ± 0.26
C_2 Phenol	1.3387	11 ± 1.8	28 ± 0.7	4.3 ± 0.36	19 ± 0.6
2,6-Dimethylphenol	1.3475	43 ± 3.3	57 ± 0.3	2.5 ± 0.11	12 ± 0.3
2,4-Dimethylphenol	1.3990	68 ± 4.3	190 ± 4	5.6 ± 0.15	40 ± 0.6
C_2 Phenol	1.4090	100 ± 5	240 ± 3	10.1 ± 0.1	44 ± 0.9
m-Ethylphenol	1.4261	210 ± 10	53 ± 0.1	0.8 ± 0.05	13 ± 0.1
2-Isopropylphenol p-Ethylphenol 3,5-Dimethylphenol	1.4510	140 ± 6	340 ± 1	1.8 ± 0.07	24 ± 0.1
3,4-Dimethylphenol	1.5202	83 ± 3.4	170 ± 3	1.8 ± 0.06	24 ± 0.3
2,4,6-Trimethylphenol	1.5573	20 ± 2.0	88 ± 0.1	9.4 ± 1.03	30 ± 1.5
C_3 Phenol	1.5639	26 ± 1.3	85 ± 1.1	2.8 ± 0.04	12 ± 0.3
C_3 Phenol	1.5816	38 ± 1.9	92 ± 1.5	3.4 ± 0.10	16 ± 0.4
C_3 Phenol	1.6043	49 ± 2.2	160 ± 1	3.9 ± 0.13	22 ± 0.3
2,3,6-Trimethylphenol	1.6137	140 ± 5	150 ± 1	2.7 ± 0.24	15 ± 0.9
C_3 Phenol	1.6287	170 ± 6	140 ± 3	1.8 ± 0.24	13 ± 0.1
C_3 Phenol	1.6685	27 ± 1.4	1000 ± 30	8.1 ± 0.11	44 ± 0.9
C_4 Phenol	1.6995	8.3 ± 0.08	61 ± 1.2	1.2 ± 0.06	2.3 ± 0.6
C_4 Phenol	1.7239	22 ± 0.5	20 ± 1.2	3.9 ± 0.12	10 ± 0.0
C_4 Phenol	1.7410	22 ± 0.9	210 ± 8	2.6 ± 0.18	nd[3]
C_4 Phenol	1.7582	10 ± 2.2	15 ± 0.5	1.8 ± 0.07	3.4 ± 0.17
C_4 Phenol	1.7847	99 ± 5.5	110 ± 3	2.0 ± 0.47	nd
C_4 Phenol	1.7886	16 ± 0.7	12 ± 1.7	2.0 ± 0.17	nd
C_5 Phenol	1.8445	11 ± 0.2	27 ± 1.0	nd[3]	3.7 ± 2.71
C_5 Phenol	1.9186	74 ± 3.8	28 ± 2.6	0.7 ± 0.05	nd
C_5 Phenol	1.9458	nd[3]	53 ± 1.6	2.1 ± 0.12	nd
C_5 Phenol	2.0133	21 ± 0.4	30 ± 0.9	nd	nd
Indanol	1.8340	130 ± 3	80 ± 2.6	1.9 ± 0.13	6.6 ± 0.28
C_1 Indanol	1.9801	39 ± 1.1	170 ± 6	1.2 ± 0.29	4.4 ± 1.32
Total Selected Phenols		2660 ± 124	4000 ± 50	93 ± 1.2	430 ± 7

[1] Relative retention times with respect to phenol.
[2] Concentrations reported as µg/mL x 10^{-2}.
[3] Concentrations reported as µg/mL.

gives Y = 1.05 + 0.257X. Both Oxy and PBC equations have larger intercepts and smaller slopes than the SRC II regression equation. Differences between log K_{bw} are less among the oils for highly substituted phenols. Differences in equations for different oils that relate log K_{bw} to phenol alkyl substitution are the result of composition of the parent oil. SRC II and Oxy contain many components that have polarities intermediate between the hydrophobic hydrocarbons and polar water. Polar constituents, such as the phenols, tend to be retained more strongly in the oil phase that more closely represents their own polarities. However, a tendency for a higher proportion of phenols from No. 2 fuel oil and PBC to enter the water column is more than compensated for by higher concentrations of phenols in Oxy and

TABLE 9. Average Phenol $\mathrm{Log}_{10}\ K_{bw}$

	PBC	Oxy	SRC II	No. 2 Fuel Oil
Phenol	1.48	1.05	0.63	nd[1]
C_1 Phenol	1.35	1.52	1.24	0.26
C_2 Phenol	1.46	1.89	1.83	0.98
C_3 Phenol	1.72	2.36	2.32	1.50
C_4 Phenol	2.17	2.14	2.55	2.00
C_5 Phenol	2.38	2.12	2.75	2.37
Indanol	1.98	2.65	2.05	1.85
C_1 Indanol	nd	1.89	2.53	1.89

[1] Not determined.

SRC II, as shown by total phenol concentrations in each WSF in Table 7. A WSF generated from SRC II contains higher concentrations of phenols than does a WSF generated from No. 2 fuel oil because, in SRC II, much larger concentrations of phenols are available to partition into the water. Phenol distribution coefficients, both oil/water and octanol/water are found in Tables 10 through 13.

Table 14 shows log K_{ow} for each degree of alkyl substitution for each oil. A linear trend from low log K_{ow} for unsubstituted phenol, to higher values with increasing alkyl substitution, is noted. This trend is graphically illustrated by plotting SRC-II log K_{ow} against alkyl substitution (Figure 16). Linear least squares treatment of SRC II phenol log K_{ow} data yields a line, $Y = 1.71 + 0.327X$, with $R^2 = 83.4$. All four oils give both measured K_{bw} and K_{ow} values for C_4 and C_5 phenols that are lower than the values calculated from their respective regression equations, probably the result of micelle formation. Regression equations for each of the oils are quite similar, indicating behavior of equivalent alkyl substituted phenols are the same for all oils. The regression equation for all phenols from all four oils is $Y = 2.01 + 0.208X$ with $R^2 = 44.5$.

Interfering hydrocarbons in the oils become a problem with analysis of more highly substituted, less polar phenols. SRC II data was plotted in Figure 16 because phenol concentrations in the oil and its WSF were higher

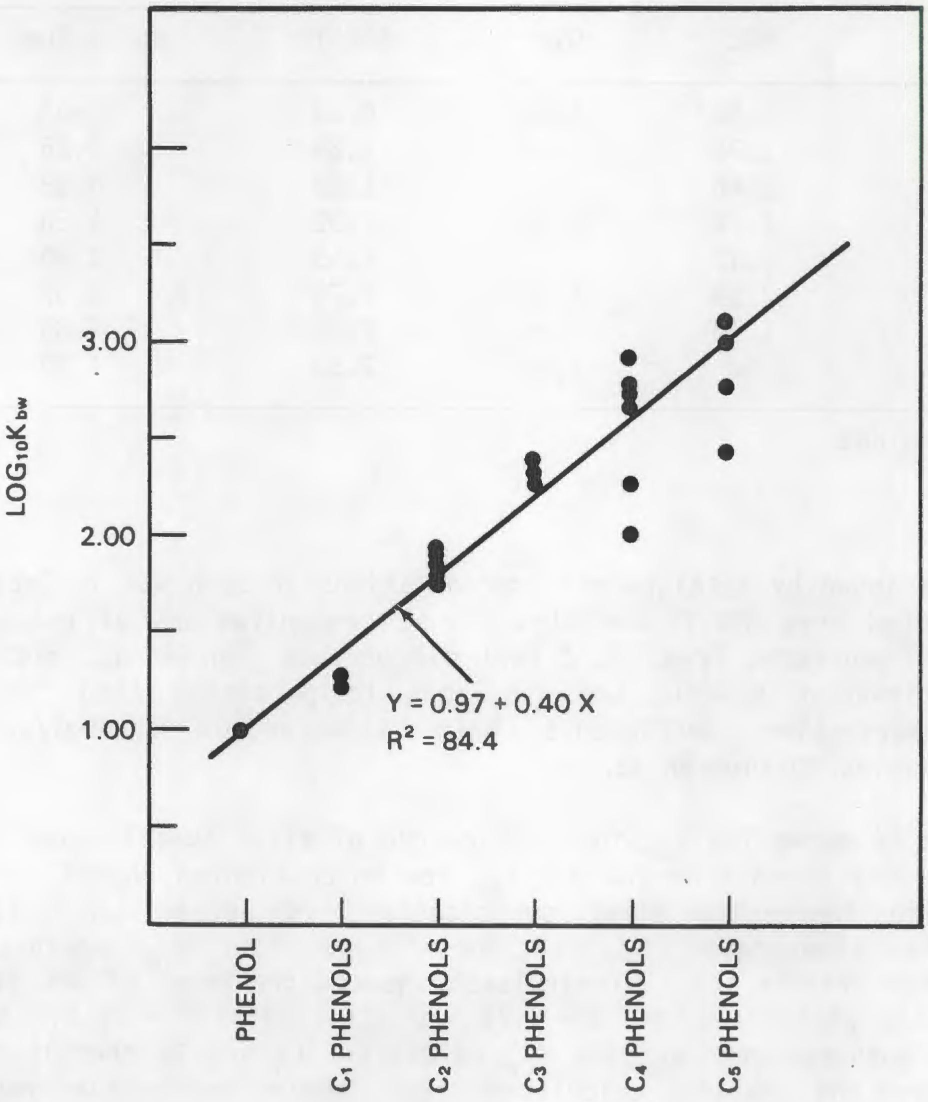

FIGURE 15. SRC II Phenol Log$_{10}$ K$_{bw}$ Plotted Against Increasing Alkyl Substitution.

TABLE 9. Average Phenol Log_{10} K_{bw}

	PBC	Oxy	SRC II	No. 2 Fuel Oil
Phenol	1.48	1.05	0.63	nd[1]
C_1 Phenol	1.35	1.52	1.24	0.26
C_2 Phenol	1.46	1.89	1.83	0.98
C_3 Phenol	1.72	2.36	2.32	1.50
C_4 Phenol	2.17	2.14	2.55	2.00
C_5 Phenol	2.38	2.12	2.75	2.37
Indanol	1.98	2.65	2.05	1.85
C_1 Indanol	nd	1.89	2.53	1.89

[1] Not determined.

SRC II, as shown by total phenol concentrations in each WSF in Table 7. A WSF generated from SRC II contains higher concentrations of phenols than does a WSF generated from No. 2 fuel oil because, in SRC II, much larger concentrations of phenols are available to partition into the water. Phenol distribution coefficients, both oil/water and octanol/water are found in Tables 10 through 13.

Table 14 shows log K_{ow} for each degree of alkyl substitution for each oil. A linear trend from low log K_{ow} for unsubstituted phenol, to higher values with increasing alkyl substitution, is noted. This trend is graphically illustrated by plotting SRC-II log K_{ow} against alkyl substitution (Figure 16). Linear least squares treatment of SRC II phenol log K_{ow} data yields a line, $Y = 1.71 + 0.327X$, with $R^2 = 83.4$. All four oils give both measured K_{bw} and K_{ow} values for C_4 and C_5 phenols that are lower than the values calculated from their respective regression equations, probably the result of micelle formation. Regression equations for each of the oils are quite similar, indicating behavior of equivalent alkyl substituted phenols are the same for all oils. The regression equation for all phenols from all four oils is $Y = 2.01 + 0.208X$ with $R^2 = 44.5$.

Interfering hydrocarbons in the oils become a problem with analysis of more highly substituted, less polar phenols. SRC II data was plotted in Figure 16 because phenol concentrations in the oil and its WSF were higher

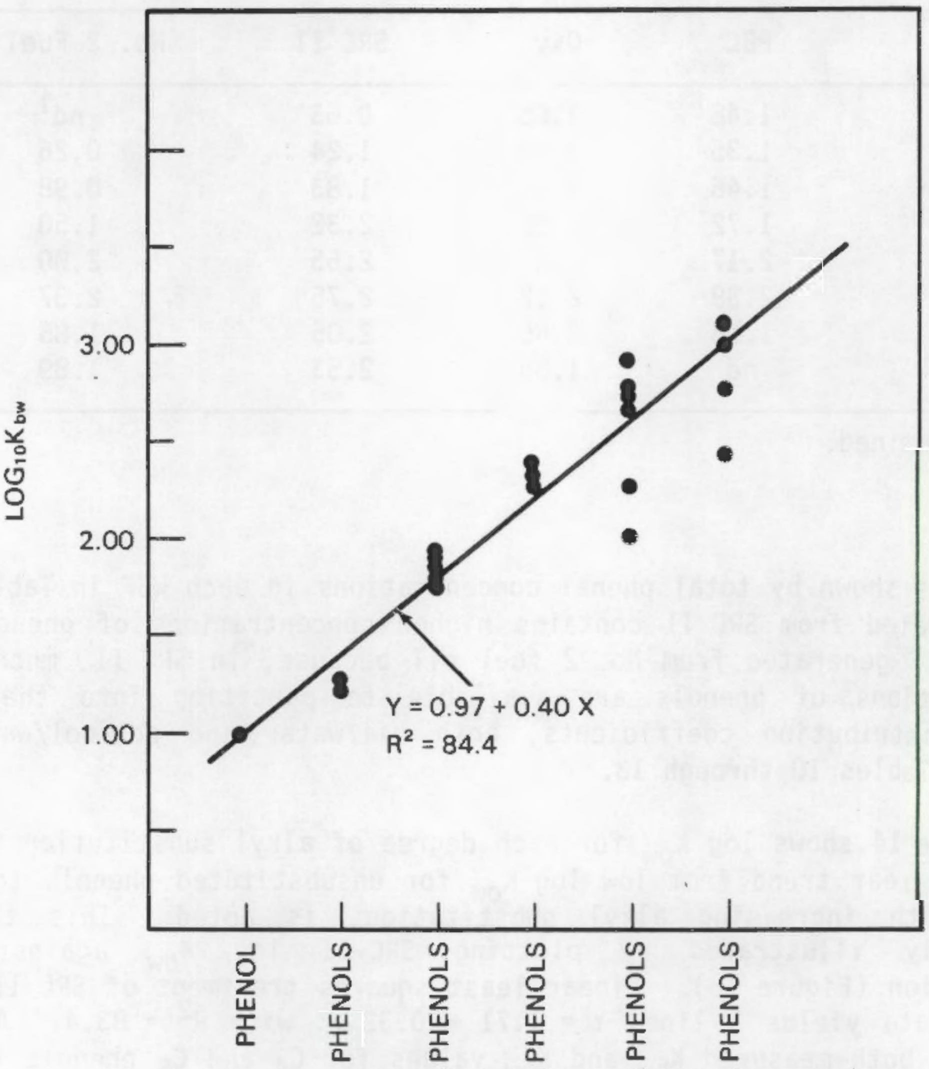

FIGURE 15. SRC II Phenol $\log_{10} K_{bw}$ Plotted Against Increasing Alkyl Substitution.

TABLE 10. SRC II Phenol Distribution Coefficients

Component	RRT[1]	Oil/Water	Log_{10} Oil/Water	Octanol/Water	Log_{10} Octanol/Water	Literature Octanol/Water[2]
Phenol	1.0000	4.2 ± 0.22	0.63	27 ± 1.8	1.43	1.46
o-Cresol	1.1754	18 ± 0.5	1.26	92 ± 6.1	1.96	1.95
m-Cresol	1.2319	17 ± 0.4	1.22	80 ± 3.4	1.90	1.96, 2.01
p-Cresol	1.2446	17 ± 0.4	1.23	80 ± 3.4	1.91	1.94, 1.92
C_2 Phenol	1.3387	83 ± 3.3	1.92	250 ± 33	2.40	
2,6-Dimethylphenol	1.3475	69 ± 1.0	1.84	290 ± 18	2.46	2.36
2,4-Dimethylphenol	1.3990	64 ± 0.5	1.81	250 ± 12	2.40	
C_2 Phenol	1.4090	65 ± 0.4	1.81	260 ± 10	2.41	
m-Ethylphenol	1.4261	60 ± 0.4	1.78	240 ± 9	2.37	2.40
2-Isopropylphenol + p-Ethylphenol + 3,5-Dimethylphenol	1.4510	55 ± 1.1	1.74	250 ± 7	2.39	2.35
3,4-Dimethylphenol	1.5202	78 ± 1.5	1.89	230 ± 9	2.36	
2,4,6-Trimethylphenol	1.5573	240 ± 18	2.38	710 ± 49	2.85	
C_3 Phenol	1.5639	210 ± 3	2.31	720 ± 33	2.85	
C_3 Phenol	1.5816	210 ± 5	2.32	700 ± 32	2.85	
C_3 Phenol	1.6043	210 ± 5	2.32	720 ± 30	2.86	
2,3,6-Trimethylphenol	1.6137	240 ± 6	2.39	840 ± 30	2.93	
C_3 Phenol	1.6287	180 ± 5	2.26	630 ± 20	2.80	
C_3 Phenol	1.6685	190 ± 9	2.29	530 ± 150	2.72	
C_4 Phenol	1.6995	190 ± 34	2.27	610 ± 13	2.79	
C_4 Phenol	1.7239	820 ± 340	2.91	2000 ± 180	3.31	
C_4 Phenol	1.7410	450 ± 63	2.65	1500 ± 72	3.18	
C_4 Phenol	1.7582	590 ± 19	2.77	1600 ± 150	3.19	
C_4 Phenol	1.7847	99 ± 2.8	2.00	1300 ± 15	2.51	
C_4 Phenol	1.7886	520 ± 270	2.72	1200 ± 50	3.06	
C_5 Phenol	1.8445	1200 ± 340	3.08	1100 ± 110	3.03	
C_5 Phenol	1.9186	270 ± 17	2.43	1100 ± 50	3.02	
C_5 Phenol	1.9458	nd[3]	nd	nd	nd	
C_5 Phenol	2.0133	560 ± 51	2.75	2400 ± 490	3.38	
Indanol	1.8340	110 ± 6	2.05	370 ± 11	2.57	
C_1 Indanol	1.9801	340 ± 17	2.53	670 ± 36	2.82	

[1] Relative retention times with respect to phenol.
[2] Reference 21.
[3] Not determined.

TABLE 11. Oxy Phenol Distribution Coefficients

Component	RRT[1]	Oil/Water	Log_{10} Oil/Water	Octanol/Water	Log_{10} Octanol/Water	Literature Octanol/Water[2]
Phenol	1.0000	11 ± 1.3	1.05	36 ± 6.4	1.56	1.46
o-Cresol	1.1754	38 ± 3.0	1.58	120 ± 15	2.09	1.95
m-Cresol	1.2319	35 ± 1.9	1.54	100 ± 9	2.01	1.96, 2.01
p-Cresol	1.2446	28 ± 1.6	1.45	110 ± 9	2.03	1.94, 1.92
C_2 Phenol	1.3387	79 ± 21.1	1.90	350 ± 99	2.55	
2,6-Dimethylphenol	1.3475	120 ± 12	2.09	400 ± 33	2.60	2.36
2,4-Dimethylphenol	1.3990	89 ± 6.6	1.95	320 ± 13	2.50	
C_2 Phenol	1.4090	90 ± 2.9	1.96	330 ± 9	2.52	
m-Ethylphenol	1.4261	55 ± 14.2	1.74	290 ± 39	2.46	2.40
2-Isopropylphenol + p-Ethylphenol + 3,5-Dimethylphenol	1.4510	66 ± 2.3	1.82	300 ± 13	2.47	2.35
3,4-Dimethylphenol	1.5202	61 ± 1.8	1.78	220 ± 19	2.34	
2,4,6-Trimethylphenol	1.5573	280 ± 22	2.45	660 ± 170	2.82	
C_3 Phenol	1.5639	290 ± 29	2.47	590 ± 189	2.77	
C_3 Phenol	1.5816	220 ± 27	2.35	530 ± 250	2.72	
C_3 Phenol	1.6043	250 ± 12	2.39	540 ± 34	2.73	
2,3,6-Trimethylphenol	1.6137	160 ± 12	2.19	630 ± 141	2.81	
C_3 Phenol	1.6287	210 ± 30	2.32	660 ± 18	2.82	
C_3 Phenol	1.6685	220 ± 8	2.35	660 ± 30	2.82	
C_4 Phenol	1.6995	78 ± 8.2	1.89	nd[3]	nd	
C_4 Phenol	1.7239	120 ± 120	2.06	170 ± 60	2.24	
C_4 Phenol	1.7410	670	2.83	520 ± 121	2.72	
C_4 Phenol	1.7582	41	1.61	nd	nd	
C_4 Phenol	1.7847	2100	3.33	180 ± 94	2.26	
C_4 Phenol	1.7886	14	1.14	300 ± 54	2.47	
C_5 Phenol	1.8445	52 ± 38	1.72	nd	nd	
C_5 Phenol	1.9186	100 ± 23	2.01	340 ± 93	2.53	
C_5 Phenol	1.9458	400 ± 195	2.59	380 ± 152	2.58	
C_5 Phenol	2.0133	140 ± 46	2.14	1120 ± 721	3.05	
Indanol	1.8340	440 ± 34	2.65	690 ± 128	2.84	
C_1 Indanol	1.9801	78 ± 16	1.89	200 ± 35	2.31	

[1] Relative retention times with respect to phenol.
[2] Reference 21.
[3] Not determined.

TABLE 12. PBC Phenol Distribution Coefficients

Component	RRT[1]	Oil/Water	Log_{10} Oil/Water	Octanol/Water	Log_{10} Octanol/Water	Literature Octanol/Water[2]
Phenol	1.0000	30 ± 14	1.48	40 ± 15	1.57	1.46
o-Cresol	1.1754	11 ± 1.6	1.04	120 ± 13	2.10	1.45
m-Cresol	1.2319	50 ± 19	1.69	110 ± 26	2.05	1.96, 2.01
p-Cresol	1.2446	22 ± 7.3	1.33	110 ± 16	2.05	1.94, 1.92
C_2 Phenol	1.3387	33 ± 8.2	1.51	320 ± 29	2.51	
2,6-Dimethylphenol	1.3475	30 ± 15	1.47	410 ± 100	2.62	2.36
2,4-Dimethylphenol	1.3990	30 ± 9.3	1.48	280 ± 41	2.45	
C_2 Phenol	1.4090	19 ± 2.6	1.28	340 ± 21	2.53	
m-Ethylphenol	1.4261	3.8 ± 8.6	1.50	290 ± 120	2.46	2.40
2-Isopropylphenol + p-Ethylphenol + 3,5-Dimethylphenol	1.4510	19 ± 8.6	1.28	390 ± 31	2.59	2.35
3,4-Dimethylphenol	1.5202	50 ± 43	1.72	410 ± 45	2.61	
2,4,6-Trimethylphenol	1.5573	61 ± 4.6	1.79	920 ± 65	2.96	
C_3 Phenol	1.5639	48 ± 5.2	1.68	980 ± 93	2.99	
C_3 Phenol	1.5816	70 ± 17	1.82	1700 ± 910	3.07	
C_3 Phenol	1.6043	52 ± 3.7	1.72	1200 ± 160	3.07	
2,3,6-Trimethylphenol	1.6137	52 ± 20	1.72	880 ± 140	2.94	
C_3 Phenol	1.6287	70 ± 33	1.83	850 ± 140	2.93	
C_3 Phenol	1.6685	33 ± 4.7	1.51	830 ± 68	2.92	
C_4 Phenol	1.6995	110 ± 17	2.05	nd	nd	
C_4 Phenol	1.7239	170 ± 54	2.22	nd	nd	
C_4 Phenol	1.7410	190 ± 94	2.29	nd	nd	
C_4 Phenol	1.7582	160 ± 27	2.20	nd	nd	
C_4 Phenol	1.7847	90 ± 11	1.97	460 ± 110	2.66	
C_4 Phenol	1.7886	200 ± 110	2.30	200 ± 79	2.31	
C_5 Phenol	1.8445	150 ± 150	2.17	nd	nd	
C_5 Phenol	1.9186	280 ± 170	2.44	180 ± 160	2.26	
C_5 Phenol	1.9458	220 ± 65	2.33	150 ± 27	2.19	
C_5 Phenol	2.0133	370 ± 170	2.56	180 ± 100	2.25	
Indanol	1.8340	95 ± 4.3	1.98	nd	nd	
C_1 Indanol	1.9801	nd[3]	nd	nd	nd	

[1] Relative retention times with respect to phenol.
[2] Reference 21.
[3] Not determined.

TABLE 13. No. 2 Fuel Oil Phenol Distribution Coefficients

Component	RRT[1]	Oil/Water	Log_{10} Oil/Water	Octanol/Water	Log_{10} Octanol/Water	Literature Octanol/Water[2]
Phenol	1.0000	nd[3]	nd	51 ± 13	1.71	1.46
o-Cresol	1.1754	2.5 ± 0.42	0.40	140 ± 10	2.15	1.95
m-Cresol	1.2319	1.9 ± 0.15	0.28	150 ± 55	2.17	1.96, 2.01
p-Cresol	1.2446	1.3 ± 0.64	0.11	120 ± 7	2.08	1.94, 1.92
C_2 Phenol	1.3387	29 ± 3.0	1.46	300 ± 68	2.48	
2,6-Dimethylphenol	1.3475	13 ± 0.9	1.11	420 ± 110	2.62	2.36
2,4-Dimethylphenol	1.3990	11 ± 0.5	1.05	350 ± 41	2.55	
C_2 Phenol	1.4090	9.0 ± 0.45	0.95	330 ± 17	2.52	
m-Ethylphenol	1.4261	4.7 ± 0.31	0.66	370 ± 87	2.56	2.40
2-Isopropylphenol + p-Ethylphenol + 3,5-Dimethylphenol	1.4510	5.7 ± 0.08	0.75	340 ± 56	2.53	2.35
3,4-Dimethylphenol	1.5202	8.2 ± 0.93	0.91	300 ± 15	2.48	
2,4,6-Trimethylphenol	1.5573	58 ± 2.6	1.76	400 ± 36	2.60	
C_3 Phenol	1.5639	31 ± 4.2	1.49	1320 ± 830	3.12	
C_3 Phenol	1.5816	28 ± 1.3	1.45	1650 ± 1250	3.22	
C_3 Phenol	1.6043	26 ± 2.5	1.42	860 ± 55	2.94	
2,3,6-Trimethylphenol	1.6137	49 ± 7.0	1.69	760 ± 120	2.88	
C_3 Phenol	1.6287	15 ± 1.1	1.17	880 ± 150	2.95	
C_3 Phenol	1.6685	31 ± 0.8	1.49	1120 ± 490	3.05	
C_4 Phenol	1.6995	170 ± 22	2.23	520 ± 350	2.72	
C_4 Phenol	1.7239	59 ± 26	1.77	nd	nd	
C_4 Phenol	1.7410	nd	nd	nd	nd	
C_4 Phenol	1.7582	nd	nd	nd	nd	
C_4 Phenol	1.7847	nd	nd	840 ± 160	2.93	
C_4 Phenol	1.7886	nd	nd	1530 ± 1140	3.19	
C_5 Phenol	1.8445	230 ± 47	2.37	nd	nd	
C_5 Phenol	1.9186	nd	nd	nd	nd	
C_5 Phenol	1.9458	nd	nd	nd	nd	
C_5 Phenol	2.0133	nd	nd	nd	nd	
Indanol	1.8340	70 ± 11	1.85	820 ± 110	2.91	
C_1 Indanol	1.9801	78 ± 5.9	1.89	nd	nd	

[1] Relative retention times with respect to phenol.
[2] Reference 21.
[3] Not determined.

TABLE 14. Average Phenol Log_{10} K_{ow}

	PBC	Oxy	SRC II	No. 2 Fuel Oil
Phenol	1.57	1.56	1.43	1.71
C_1 Phenol	2.07	2.04	1.92	2.13
C_2 Phenol	2.54	2.49	2.40	2.53
C_3 Phenol	2.98	2.78	2.84	2.97
C_4 Phenol	2.49	2.42	3.01	2.95
C_5 Phenol	2.23	2.72	3.14	nd
Indanol	nd[1]	2.84	2.57	2.91
C_1 Indanol	nd	2.31	2.82	nd

[1] Not determined.

than concentrations in each other oil and its WSF, so that fewer interferences were encountered in quantification of phenol components in SRC II aqueous and nonaqueous phases. Some analytical interference problems could be overcome by hydrolyzing derivatized phenols in base and performing an additional solvent wash of the aqueous phenol sodium salts before rederivatization, extraction, and analysis. This, however, would result in significant loses, would require a considerably more time consuming extraction procedure, and would require recalibration of the method.

NITROGEN BASES

The total concentrations of nitrogen bases vary widely among the four oils studied. This is to be expected because synthetic oils and petroleum oils are created through very different processes using different starting materials. The synthetic fuels contain considerably larger quantities of basic nitrogen components. Concentrations of water-solubilized nitrogen bases in each of the four oils are summarized in Table 15. Concentrations of total nitrogen bases range from 94 µg/mL in No. 2 fuel oil, 1200 µg/mL in Oxy, to 20,000 µg/mL in SRC II. Some nitrogen bases were observed in PBC but their concentrations were too low to quantify. Table 16 shows TOC concentrations for a WSF of each oil, total selected nitrogen base concentrations in each oil, and total nitrogen base concentrations in each WSF. SRC II contained slightly more than 2% water-soluble basic nitrogen components, while Oxy consisted of slightly more than 0.1% and No. 2 fuel

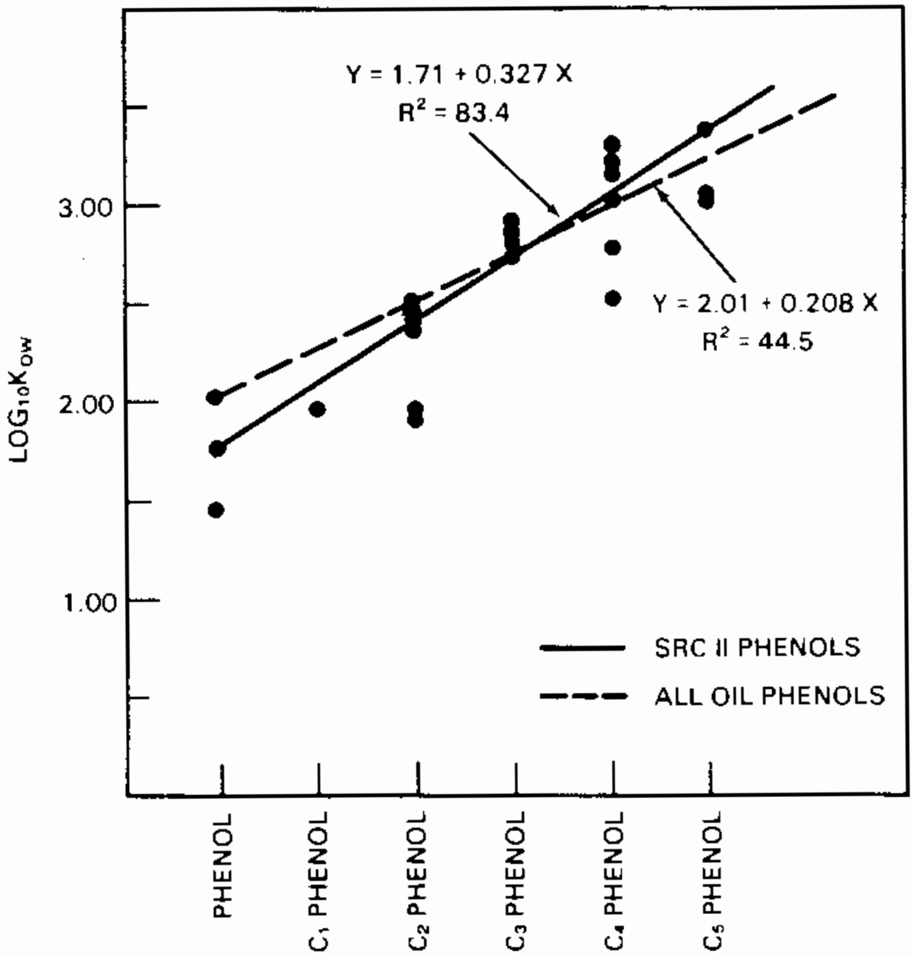

FIGURE 16. SRC II Phenol Log_{10} K_{ow} Plotted Against Increasing Alkyl Substitution.

TABLE 15. Nitrogen Base Concentrations in Oils

Component	RRT[1]	SRC II[2]	Oxy[2]	No. 2 Fuel Oil[3]
C_2 Pyridine	0.9132	nd[3]	nd	nd
Aniline	1.0000	2100 ± 210	nd	nd
C_3 Pyridine	1.1062	140 ± 18	70 ± 2	nd
C_4 Aniline	1.4223	3800 ± 360	nd	nd
C_4 Aniline	1.4469	1800 ± 170	nd	nd
C_4 Pyridine	1.6218	93 ± 30	10 ± 1.5	nd
C_2 Aniline	1.8666	1400 ± 120	nd	10 ± 2.3
C_2 Aniline	1.8938	1600 ± 140	11 ± 1.0	10 ± 1.9
C_2 Aniline	1.9106	3900 ± 38	49 ± 3.9	4 ± 1.2
C_2 Aniline	2.0155	260 ± 42	9 ± 1.4	3.8 ± 0.88
Quinoline	2.2034	1800 ± 190	73 ± 2.5	9.2 ± 0.99
Isoquinoline + C_3 Aniline	2.3096	870 ± 100	49 ± 1.3	5 ± 1.2
C_1 Quinoline	2.5389	2000 ± 290	110 ± 6	6 ± 1.2
C_1 Quinoline	2.7370	1100 ± 100	57 ± 3.8	8 ± 1.5
C_1 Quinoline	2.7642	1500 ± 140	39 ± 5.1	7 ± 1.0
C_1 Quinoline	2.9326	470 ± 29	170 ± 13	6 ± 1.0
C_2 Quinoline	3.0440	1200 ± 190	290 ± 21	9 ± 1.5
C_3 Quinoline	3.6062	150 ± 12	280 ± 65	nd
Total Selected Nitrogen Bases		20000 ± 1400	1200 ± 60	90 ± 18

[1] Relative retention times with respect to aniline.
[2] Concentrations reported in μg/mL.
[3] Not determined.

TABLE 16. Total Nitrogen Base Concentrations in Oils and Their Corresponding WSF (μg/mL)

Oil Type	Nitrogen Base Conc. in Oil	Nitrogen Base Conc. in WSF	TOC
SRC II	20000 ± 1300	64 ± 10	4400 ± 290
Oxy	1200 ± 60	2.3 ± 0.4	310 ± 4
PBC	nd[1]	nd	26 ± 1
No. 2 Fuel Oil	90 ± 18	0.41 ± 0.02	120 ± 8

[1] Not determined.

oil contained only about 0.01% nitrogen bases. Each nitrogen base WSF was generated from a 1:10 oil in water (v:v) ratio; concentrations of nitrogen bases ranged from barely detectable quantities in a PBC WSF to more than 63 μg/mL in an SRC II WSF. Oxy and No. 2 fuel oil WSF concentrations were intermediate with slightly less than 2.3 μg/mL and 0.41 μg/mL, respectively. Correspondingly, TOC values followed the same concentration trend with a low of 26 μg/mL for PBC and 120 μg/mL, 310 μg/mL, and 4370 μg/mL for No. 2 fuel oil, Oxy, and SRC II, respectively. Total organic carbon analyses measure water-solubilized nitrogen bases, in addition to all other organic components present in each WSF.

Figure 17 shows NPD chromatograms of a WSF from each oil. Anilines and quinolines constituted the majority of basic nitrogen components in SRC II, with pyridines contributing only slightly to the total basic nitrogen concentration. Pyridines are present in Oxy, but they are relatively more volatile than anilines and quinolines. Therefore, because Oxy is quite viscous at room temperature and contains few of the more volatile components, pyridines are not seen in high concentrations. No. 2 fuel oil also has only traces of pyridine components.

Table 17 summarizes log K_{bw} for each oil type. Nitrogen base K_{bw} are lowest for No. 2 fuel oil, higher for Oxy, and highest for SRC II. Regression analyses of log K_{bw} for quinoline data on degree of alkyl substitution yield the intercepts 1.29 for No. 2 fuel oil, 1.85 for Oxy, and 2.99 for SRC II. However, because the slope of the regression lines is lowest for SRC II and highest for No. 2 fuel oil, differences in K_{bw} for substituted quinolines are smaller among the oils than are differences in K_{bw} for unsubstituted quinolines. Figure 18 shows SRC II log K_{bw} for nitrogen bases plotted against increasing alkyl substitution. A linear trend is observed in partitioning behavior of nitrogen bases with alkyl substitution; more alkyl substitution causes greater partitioning into the oil phase. Tables 18 through 20 show K_{bw} and K_{ow} calculated for nitrogen bases.

Nitrogen base K_{ow} are tabulated for components of equivalent alkyl substitution and are shown in Table 21. Data generated in this study show that the presence of components other than nitrogen bases in the aqueous samples do not cause K_{ow} values to deviate appreciably from literature values. Campbell et al. (15) measured K_{ow} for aniline and pyridine both from single solute solutions and from a complex coal gasification waste water that had been spiked with aniline and pyridine and found no differences. For the most part, K_{ow} data calculated in this study reproduce literature values quite closely. The source material oil

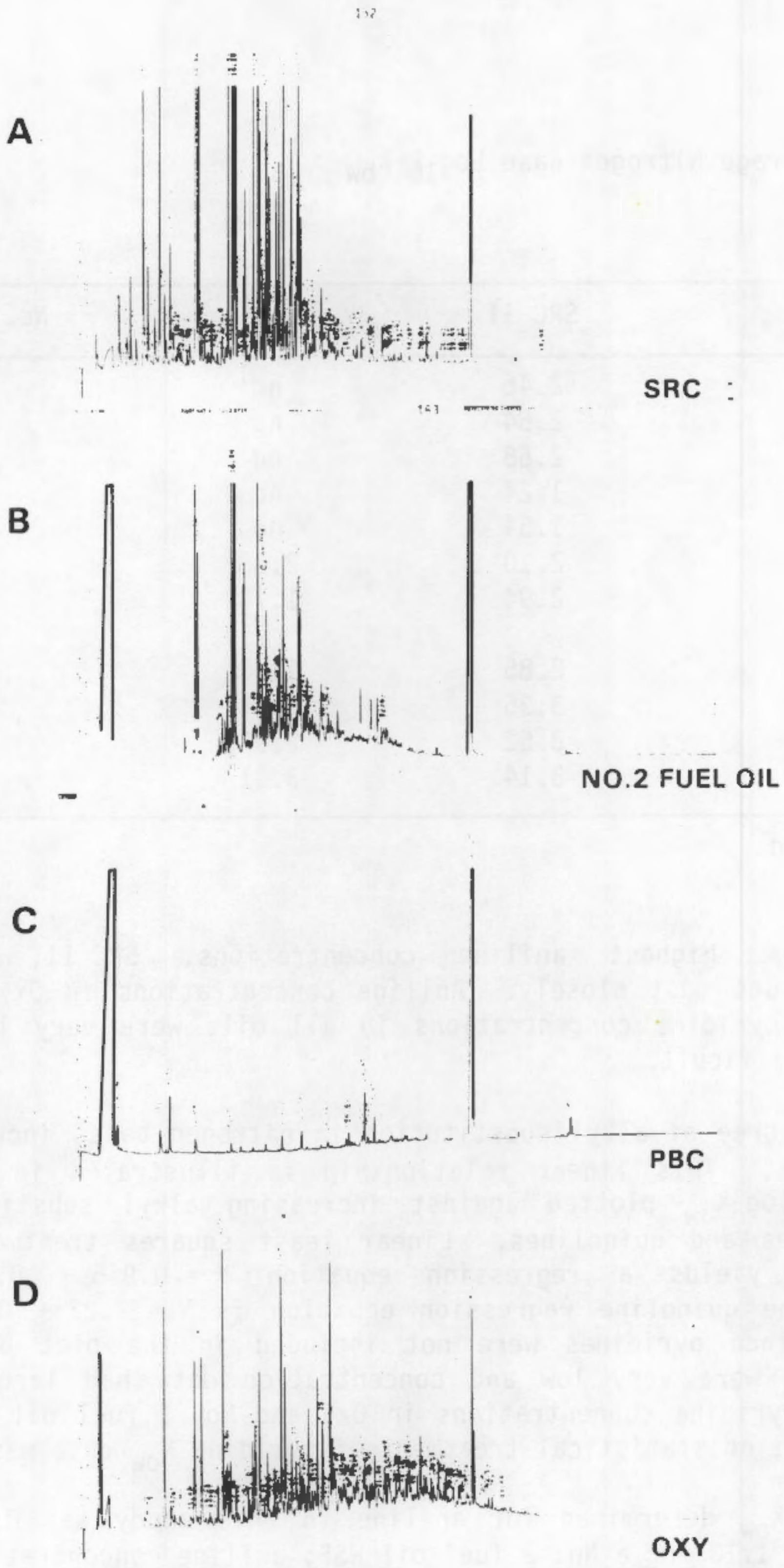

FIGURE 17. Gas Chromatograms of WSF Nitrogen Base Fraction (A) SRC II (B) No. 2 Fuel Oil (C) PBC (D) Oxy

TABLE 17. Average Nitrogen Base $\mathrm{Log}_{10}\ K_{bw}$

	SRC II	Oxy	No. 2 Fuel Oil
C_2 Pyridine	2.46	nd[1]	nd
C_3 Pyridine	2.54	nd	nd
C_4 Pyridine	2.68	nd	nd
Aniline	1.24	nd	1.03
C_1 Aniline	1.54	nd	nd
C_2 Aniline	2.10	2.38	0.97
Quinoline	2.94	1.70	1.22
Isoquinoline + C_3 Aniline	2.85	2.40	1.39
C_1 Quinoline	3.36	2.36	1.88
C_2 Quinoline	3.62	2.93	2.34
C_3 Quinoline	3.14	3.11	nd

[1] Not determined.

containing the highest aniline concentrations, SRC II, reproduced literature values most closely. Aniline concentrations in Oxy and No. 2 fuel oil and pyridine concentrations in all oils were very low, making quantitation difficult.

As the degree of alkyl substitution in nitrogen bases increases, K_{ow} also increases. This linear relationship is illustrated in Figure 19, which shows log K_{ow} plotted against increasing alkyl substitution for SRC II anilines and quinolines. Linear least squares treatment of the aniline data yields a regression equation $Y = 0.966 + 0.448X$ with $R^2 = 96.6$. The quinoline regression equation is $Y = 2.22 + 0.425X$ with $R^2 = 86.1$. Since pyridines were not included in the plot because oil concentrations were very low and concentration data had large standard deviations. Pyridine concentrations in Oxy and No. 2 fuel oil were lower than in SRC II, no statistical treatment of pyridine K_{ow} data was possible.

The log K_{ow} determined for aniline in this study was 0.96 for an SRC II WSF and 1.13 for a No. 2 fuel oil WSF; aniline concentrations in Oxy were too low to quantify, so no K_{ow} data is available. The differences between K_{ow} for aniline and C_2-substituted aniline show there is a large

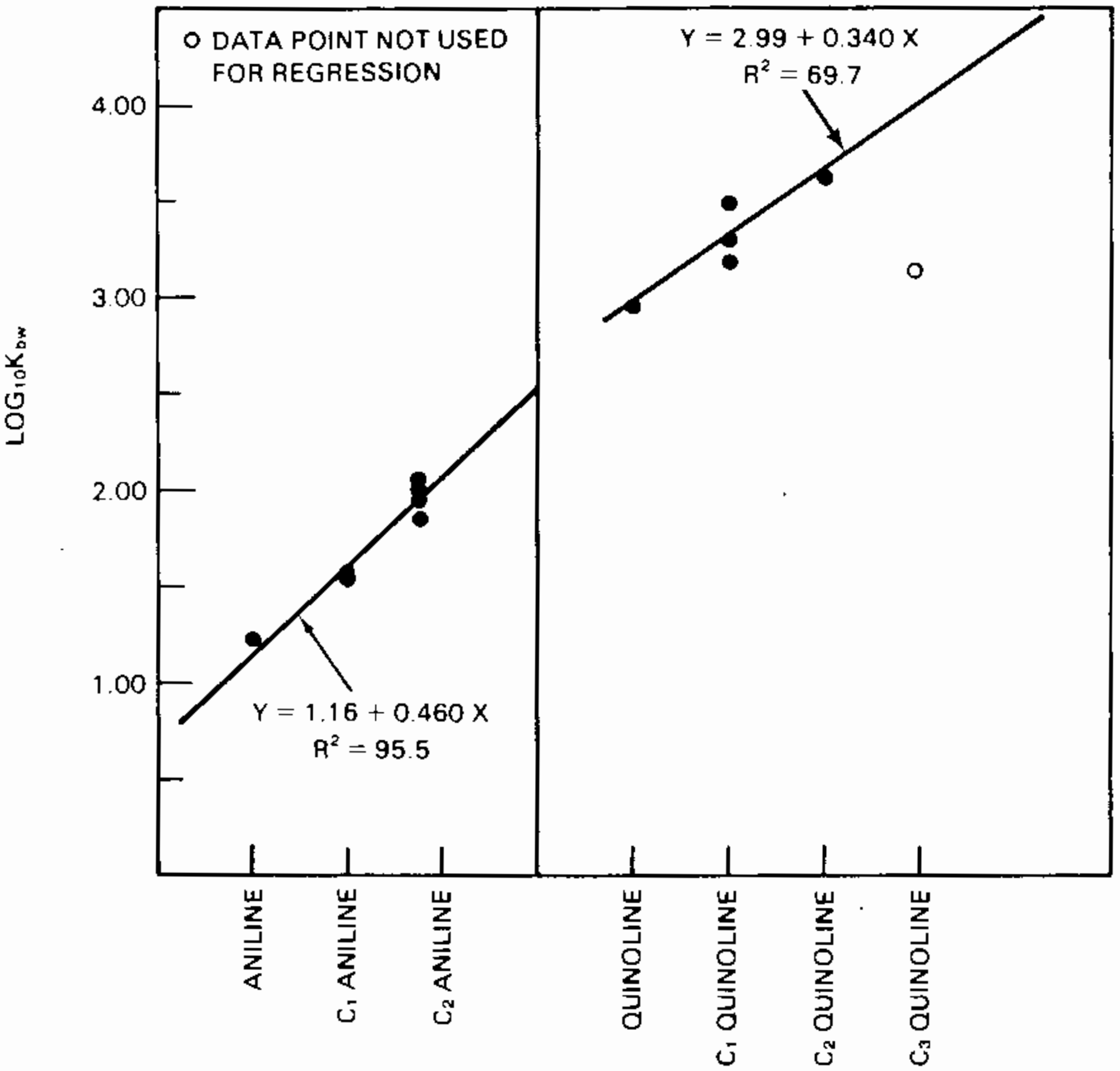

FIGURE 18. SRC II Nitrogen Base Log_{10} K_{bw} Plotted Against Increasing Alkyl Substitution. [C_3 quinoline concentrations in oil and aqueous phases were very low so the distribution coefficient is not reliable so it was not used in the regression analysis.]

TABLE 18. SRC II Nitrogen Base Distribution Coefficients

Component	RRT[1]	Oil/Water	Log_{10} Oil/Water	Octanol/Water	Log_{10} Octanol/Water	Literature Octanol/Water[2]
C_2 Pyridine	0.9132	290 ± 46	2.46	50 ± 8	1.71	
Aniline	1.0000	20 ± 4	1.24	9 ± 1.3	0.96	0.90, 0.98
C_3 Pyridine	1.1062	350 ± 49	2.54	40 ± 6.0	1.60	2.36, 1.95, 2.10, 1.72
C_1 Aniline	1.4223	30 ± 6	1.53	25 ± 3.0	1.40	1.40, 1.43, 1.29
C_1 Aniline	1.4469	40 ± 6	1.54	28 ± 2.9	1.44	1.32, 1.39, 1.41
C_4 Pyridine	1.6218	500 ± 540	2.68	13 ± 1.7	1.12	
C_2 Aniline	1.8666	110 ± 13	2.03	78 ± 8.5	1.89	1.85, 1.70
C_2 Aniline	1.8938	120 ± 14	2.09	77 ± 8.4	1.88	
C_2 Aniline	1.9106	140 ± 14	2.16	86 ± 9.2	1.93	
C_2 Aniline	2.0155	130 ± 48	2.11	55 ± 5.7	1.74	
Quinoline	2.2034	870 ± 93	2.94	170 ± 17	2.24	2.03, 2.06
Isoquinoline + C_3 Aniline	2.3096	710 ± 69	2.85	210 ± 29	2.32	2.08
C_1 Quinoline	2.5389	1960 ± 220	3.29	400 ± 42	2.60	2.57, 2.47, 2.60
C_1 Quinoline	2.7370	1500 ± 180	3.18	300 ± 31	2.47	
C_1 Quinoline	2.7642	3050 ± 350	3.48	540 ± 130	2.74	
C_1 Quinoline	2.9326	3050 ± 410	3.48	500 ± 170	2.70	
C_2 Quinoline	3.0440	4200 ± 610	3.62	1240 ± 650	3.09	
C_3 Quinoline	3.6062	1380 ± 160	3.14	250 ± 85	2.39	

[1] Relative retention times with respect to aniline.
[2] Reference 21.

TABLE 19. Oxy Nitrogen Base Distribution Coefficients

Component	RRT[1]	Oil/Water	Log_{10} Oil/Water	Octanol/Water	Log_{10} Octanol/Water	Literature Octanol/Water[2]
C_2 Pyridine	0.9132	nd[3]	nd	nd	nd	
Aniline	1.0000	nd	nd	nd	nd	0.90, 0.98
C_3 Pyridine	1.1062	nd	nd	22 ± 2.9	1.34	2.36, 1.95, 2.10, 1.72
C_1 Aniline	1.4223	nd	nd	50 ± 8.3	1.70	1.40, 1.43, 1.29 1.32, 1.39, 1.41
C_1 Aniline	1.4469	nd	nd	140 ± 240	2.16	
C_4 Pyridine	1.6218	nd	nd	220 ± 99	2.35	
C_2 Aniline	1.8666	nd	nd	90 ± 16	1.97	1.85, 1.70
C_2 Aniline	1.8938	260 ± 24	2.42	nd	nd	
C_2 Aniline	1.9106	200 ± 17	2.30	170 ± 29	2.24	
C_2 Aniline	2.0155	260 ± 48	2.41	250 ± 46	2.40	
Quinoline	2.2034	50 ± 5.4	1.70	90 ± 15	1.96	2.03, 2.06
Isoquinoline + C_3 Aniline	2.3096	250 ± 19	2.40	230 ± 25	2.36	2.08
C_1 Quinoline	2.5389	110 ± 15	2.06	190 ± 21	2.28	2.57, 2.47, 2.60
C_1 Quinoline	2.7370	360 ± 52	2.56	480 ± 42	2.68	
C_1 Quinoline	2.7642	190 ± 28	2.27	240 ± 27	2.38	
C_1 Quinoline	2.9326	350 ± 59	2.54	320 ± 27	2.51	
C_2 Quinoline	3.0440	850 ± 180	2.93	270 ± 20	2.44	
C_3 Quinoline	3.6062	1300 ± 230	3.11	840 ± 670	2.93	

[1] Relative retention times with respect to aniline.
[2] Reference 21.
[3] Not determined.

TABLE 20. No. 2 Fuel Oil Nitrogen Base Distribution Coefficients

Component	RRT[1]	Oil/Water	$\log_{10}$ Oil/Water	Octanol/Water	$\log_{10}$ Octanol/Water	Literature Octanol/Water[2]
C_2 Pyridine	0.9132	nd[3]	nd	nd	nd	
Aniline	1.0000	11 ± 0.6	1.03	14 ± 3.3	1.13	0.90, 0.98
C_3 Pyridine	1.1062	nd	nd	nd	nd	2.36, 1.95, 2.10, 1.72
C_1 Aniline	1.4223	2.4 ± 0.30	0.38	8 ± 1.9	0.90	1.40, 1.43, 1.29, 1.32, 1.39, 1.41
C_1 Aniline	1.4469	nd	nd	nd	nd	
C_4 Pyridine	1.6218	nd	nd	nd	nd	
C_2 Aniline	1.8666	10 ± 1.2	1.00	31 ± 6.5	1.49	1.85, 1.70
C_2 Aniline	1.8938	10 ± 1.2	1.00	21 ± 4.7	1.32	
C_2 Aniline	1.9106	14 ± 2.0	1.14	13 ± 3.3	1.12	
C_2 Aniline	2.0155	6 ± 1.5	0.75	20 ± 17	1.38	
Quinoline	2.2034	17 ± 1.2	1.22	70 ± 17	1.87	2.03, 2.06
Isoquinoline + C_3 Aniline	2.3096	24 ± 2.8	1.39	60 ± 28	1.79	2.08
C_1 Quinoline	2.5389	37 ± 9.6	1.57	130 ± 27	2.12	2.57, 2.47, 2.60
C_1 Quinoline	2.7370	90 ± 17.6	1.97	280 ± 76	2.45	
C_1 Quinoline	2.7642	70 ± 10	1.82	180 ± 37	2.25	
C_1 Quinoline	2.9326	150 ± 39	2.17	87 ± 48	1.94	
C_2 Quinoline	3.0440	220 ± 67	2.34	190 ± 110	2.29	
C_3 Quinoline	3.6062	nd	nd	nd	nd	

[1] Relative retention times with respect to aniline.
[2] Reference 21.
[3] Not determined.

TABLE 21. Average Nitrogen Base $\log_{10} K_{ow}$

	SRC II	Oxy	No. 2 Fuel Oil
C_2 Pyridine	1.71	nd[1]	nd
C_3 Pyridine	1.60	1.34	nd
C_4 Pyridine	1.12	2.35	nd
Aniline	0.96	nd	1.13
C_1 Aniline	1.42	1.93	0.90
C_2 Aniline	1.86	2.20	1.33
Quinoline	2.24	1.96	1.87
Isoquinoline + C_3 Aniline	2.32	2.36	1.79
C_1 Quinoline	2.63	2.46	2.19
C_2 Quinoline	3.09	2.44	1.94
C_3 Quinoline	2.39	2.93	2.29

[1] Not determined.

increase in lipid solubility with increasing substitution. Anilines of the same molecular weights as pyridines have lower K_{ow} than do the pyridines, because anilines, which are primary amines, have less alkyl substitution for a given molecular weight than do pyridines which are heterocyclic basic compounds.

Quinoline and alkyl quinoline K_{ow} calculated from each oil WSF in this study were slightly lower than published values. However, in the case of SRC II and Oxy, these log K_{ow} differed from literature values by less than 10%. No. 2 fuel oil provided data that varied from literature data by as much as 20%, but these deviations could probably be accounted for by extremely low concentrations of nitrogen bases and by the presence of analytical interferences, rather than by interactions of nitrogen bases and other sample components.

SATURATED AND AROMATIC HYDROCARBONS

Aromatic and saturated hydrocarbons are present in all four oils studied and in each WSF. These hydrocarbons are relatively nonpolar and tend not to partition into aqueous phases to very high concentrations, thus

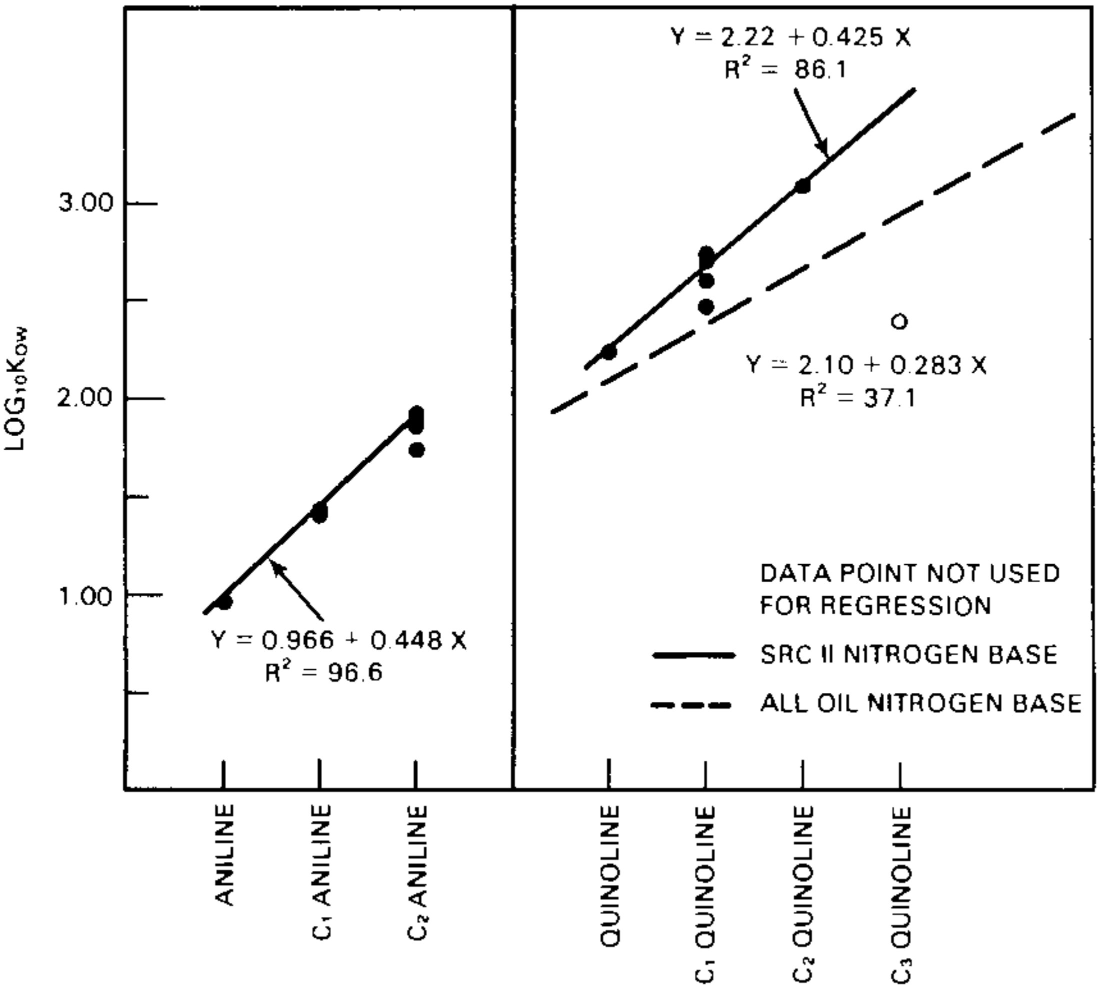

FIGURE 19. SRC II Nitrogen Base Log_{10} K_{ow} Plotted Against Increasing Alkyl Substitution. [C_3 quinoline concentrations in oil and aqueous phases were very low so the distribution coefficient is not reliable so it was not used in the regression analysis.]

creating analytical difficulties. The procedures used must be able to detect and quantify concentrations at the μg/L level.

Saturated hydrocarbons are highly nonpolar so as to have exceedingly low water solubilities. Even taking into account the phenomenon of "accomodation," (95) or the creation of aggregates of molecules in aqueous suspension, WSF concentrations are very low. Filtration of a WSF removes nearly all saturated hydrocarbons (96), indicating accomodation is the primary means by which aliphatic hydrocarbons enter the water column. This fact may explain why concentrations of saturated hydrocarbons in aqueous samples vary by as much as 20% for replicate samples. The presence of aggregates of molecules make it difficult to obtain a homogeneous WSF. Saturated hydrocarbons have been quantified in whole oils, oil phases, and aqueous phases resulting from oil/water equilibration. Octanol phases were not quantified because octanol created serious chromatographic interference problems and because aqueous phases following equilibration with octanol contained concentrations of individual aliphatic components that were too low for measurement in this study. Because saturated hydrocarbons are highly water insoluble and because little toxological work has been conducted using them as source materials, the analysis of the aliphatic constituents was not pursued beyond determination of their concentrations in whole oils and the oil and aqueous phases resulting from generation of each WSF.

Concentrations of total C_8 through C_{26} saturated hydrocarbons varied considerably among the four source material oils, as is shown in Table 22. This table also shows TOC concentrations in each oil WSF and total concentrations of saturated hydrocarbons in the oil WSF. No. 2 fuel oil contains relatively greater concentrations of saturated hydrocarbons than do Oxy, PBC, or SRC II, with saturated hydrocarbons accounting for approximately 14% of the petroleum distillate. In Oxy, PBC, and SRC II, saturated hydrocarbons account for slightly more than 8%, 5.5%, and 2%, respectively. Concentrations of saturated hydrocarbons are shown in Table 23 for each of the four oils. Concentrations of the saturated components vary with their volatility among the different oils. This is illustrated in the chromatograms in Figure 20. Included with chromatograms of saturated hydrocarbons for each of the oils is a chromatogram of C_8 through C_{26} standard aliphatic hydrocarbons. Few volatile components are present in Oxy. No. 2 fuel oil saturated hydrocarbons show a concentration increase to a maximum of sixteen carbon atoms and decreasing concentrations of larger aliphatic hydrocarbons.

TABLE 22. Total Saturated Hydrocarbon Concentrations in Oils and Their Corresponding WSF (μg/mL)

Oil Type	Saturated Hydrocarbon Conc. in Oil	Saturated Hydrocarbon Conc. in WSF	TOC
SRC II	17000	0.18	4400 ± 290
Oxy	84000 ± 3300	nd[1]	310 ± 4
PBC	55000 ± 100	0.04 ± 0.00	26 ± 1
No. 2 Fuel Oil	140000 ± 1000	0.7 ± 0.4	120 ± 8

[1] Not determined.

TABLE 23. Saturated Hydrocarbon Concentrations in Oils

Component	RRT[1]	SRC II[2]	Oxy[2]	PBC[2]	No. 2 Fuel Oil[2]
C_8	0.2588	95 ± 6	nd[3]	2740 ± 180	490 ± 32
C_9	0.3528	370 ± 6	35 ± 1	3550 ± 50	1820 ± 120
C_{10}	0.4641	1000 ± 48	160 ± 8	3650 ± 110	5280 ± 300
C_{11}	0.5795	1760 ± 38	540 ± 29	3470 ± 110	8930 ± 140
C_{12}	0.6924	2250 ± 200	1420 ± 49	3200 ± 50	10400 ± 100
C_{13}	0.8006	2410 ± 83	2510 ± 38	3700 ± 50	10900 ± 80
C_{14}	0.9030	2620 ± 110	3520 ± 60	3280 ± 10	11900 ± 100
C_{15}	1.0000	2200 ± 45	4080 ± 130	2760 ± 380	12900 ± 150
C_{16}	1.0917	1760 ± 50	4390 ± 220	2660 ± 40	13900 ± 200
C_{17}	1.1788	930 ± 19	5510 ± 300	3250 ± 210	13700 ± 280
Pristane	1.1789	290 ± 15	5970 ± 330	2080 ± 230	4750 ± 120
C_{18}	1.2616	550 ± 23	4800 ± 240	1600 ± 70	11900 ± 240
Phytane	1.2703	nd[3]	3880 ± 220	800 ± 50	4200 ± 80
C_{19}	1.3402	390 ± 9	5810 ± 270	1640 ± 160	10600 ± 210
C_{20}	1.4152	350 ± 16	6460 ± 290	1940 ± 270	9000 ± 80
C_{21}	1.4869	240 ± 96	6130 ± 230	1920 ± 310	4650 ± 60
C_{22}	1.5552	200 ± 14	5500 ± 140	1960 ± 290	2650 ± 70
C_{23}	1.6207	nd	5280 ± 250	1990 ± 360	1400 ± 60
C_{24}	1.6840	nd	5990 ± 140	2990 ± 430	440 ± 29
C_{25}	1.7493	nd	7670 ± 1070	2410 ± 1040	nd
C_{26}	1.8193	nd	4000 ± 400	1490 ± 60	nd
Total Selected Saturated Hydrocarbons		17000	84000 ± 3300	55000 ± 100	140000 ± 1,000

[1] Relative retention times with respect to C_{15}.
[2] Concentrations reported in μg/mL.
[3] Not determined.

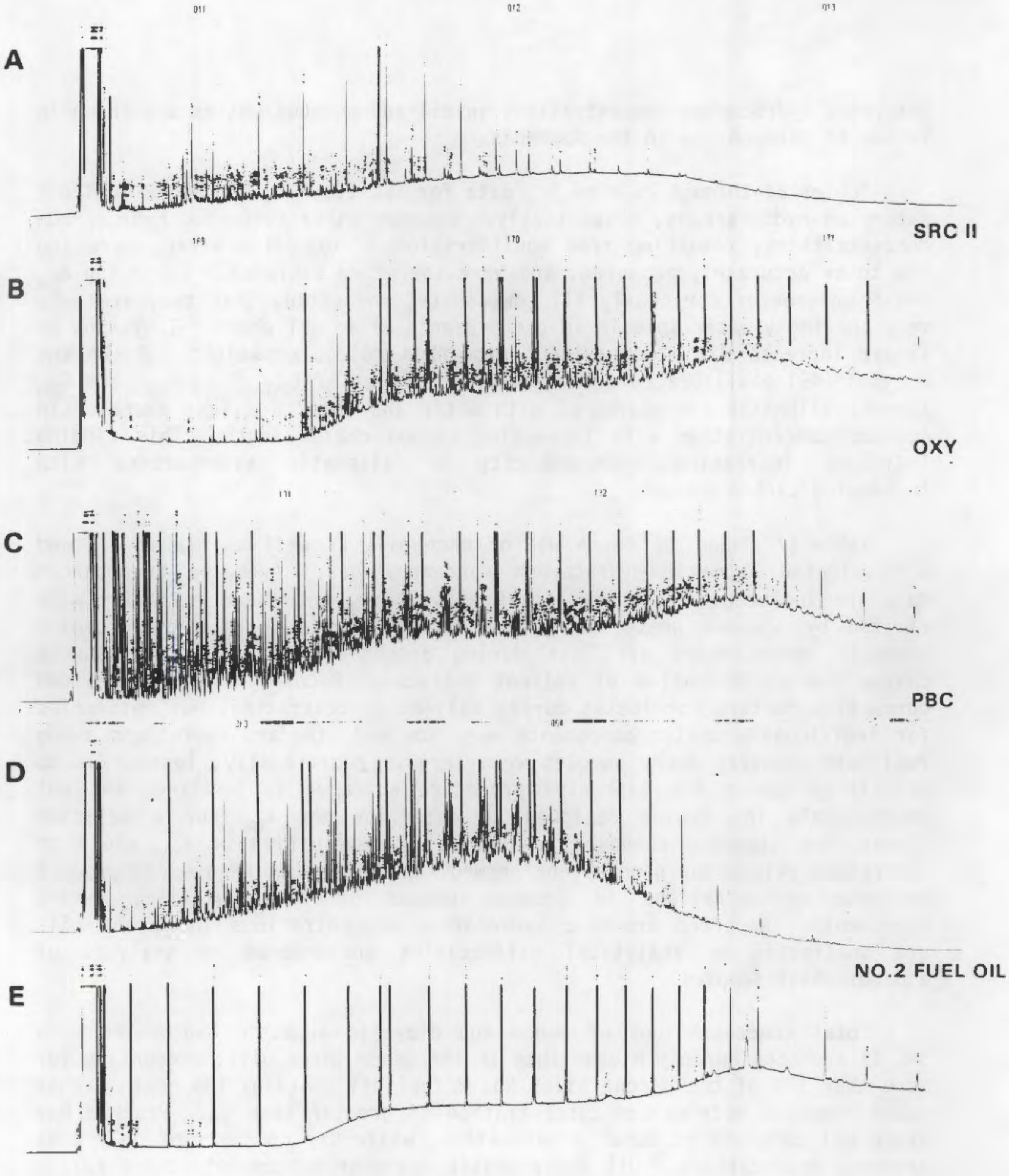

FIGURE 20. Gas Chromatograms of Saturated Hydrocarbons (A) SRC II (B) Oxy (C) PBC (D) No. 2 Fuel Oil (E) Standard Mix.

Saturated hydrocarbon concentrations in oil and aqueous phases are shown in Tables 8A through 11A in the Appendix.

Tables 24 through 26 show K_{bw} data for SRC II, PBC, and No. 2 fuel oil saturated hydrocarbons, respectively. Aqueous phase saturated hydrocarbon concentrations, resulting from equilibration of Oxy with water, were too low to be accurately measured, and were therefore excluded. These log K_{bw} are 5 or greater for nearly all components, indicating that they are only very sparingly water soluble in the presence of an oil phase. They show no linear increase with increasing hydrocarbon molecular weight. Peake and Hodgson (49) equilibrated equal numbers of moles of C_{20}, C_{22}, C_{24}, and C_{28} (normal aliphatic hydrocarbons) with water and found a slight decrease in aqueous concentration with increasing carbon chain length. This finding indicates increasing hydrophobicity of aliphatic hydrocarbons with increasing carbon number.

Table 27 shows TOC for a WSF of each oil, as well as parent oil and WSF selected aromatic hydrocarbon concentrations. Aromatic hydrocarbon data are included in the results of this study, but their reliability is limited by aqueous phase analytical difficulties. Volatile, monocyclic aromatic hydrocarbons are lost during procedural siphoning of aqueous phases and concentration of solvent extracts. Recovery studies provided correction factors for losses during solvent concentration, but recoveries for individual aromatic components were low and standard deviations among replicate recovery study samples were large. Additionally, losses due to volatility during the siphoning procedure appeared to be large and not reproducible in studies designed to determine the K_{ow} for a selected single-ring standard compound, o-xylene. Determination of K_{ow} close to literature values for naphthalene showed the method can be used to produce accurate concentrations in aqueous phases of less volatile, 2-ring components. Reported aromatic hydrocarbon concentrations in parent oils are unaffected by analytical difficulties encountered in analysis of aqueous phase samples.

Total concentrations of mono- and dicyclic aromatic hydrocarbons in SRC II are considerably higher than in the other three oils, accounting for more than 17% of the parent oil. No. 2 fuel oil contains the next largest total aromatic hydrocarbon concentration of greater than 5%. Prudhoe Bay Crude oil consists of about 2% aromatics, while Oxy consists of only 1.6% aromatic hydrocarbons. Oil WSF aromatic hydrocarbon concentrations follow a similar order, with the only change in concentration order being a reversal of PBC and Oxy. Figure 21 shows aromatic hydrocarbon gas chromatograms generated by a WSF of each oil, and Table 28 shows

TABLE 24. SRC II Saturated Hydrocarbon Distribution Coefficients

Component	RRT[1]	Oil/Water x 10^3	Log_{10} Oil/Water
C_8	0.2588	130 ± 22	5.10
C_9	0.3528	94 ± 8	4.97
C_{10}	0.4641	101 ± 8	5.00
C_{11}	0.5795	109 ± 8	5.04
C_{12}	0.6924	90 ± 13	4.96
C_{13}	0.8006	100 ± 13	5.01
C_{14}	0.9030	110 ± 12	5.02
C_{15}	1.0000	100 ± 15	4.99
C_{16}	1.0917	90 ± 19	4.93
C_{17}	1.1788	90 ± 11	4.94
Pristane	1.1789	100 ± 13	4.98
C_{18}	1.2616	90 ± 20	4.94
Phytane	1.2703	nd[2]	nd
C_{19}	1.3402	100 ± 15	5.00
C_{20}	1.4152	100 ± 16	5.02
C_{21}	1.4869	100 ± 17	5.02
C_{22}	1.5552	200 ± 109	5.26
C_{23}	1.6207	nd	nd
C_{24}	1.6840	nd	nd
C_{25}	1.7493	nd	nd
C_{26}	1.8193	nd	nd

[1] Relative retention times with respect to C_{15}.
[2] Not determined.

concentrations of aromatic components determined for each of the four oils. Tables 12A through 15A, in the Appendix, show concentrations of aromatic hydrocarbons in oils and aqueous phases for all oils.

Table 29 shows average log K_{bw} for positional isomers of equivalent alkyl substitution measured for each of the four oils. Unsubstituted naphthalene and C_2 benzenes have similar K_{bw} in each oil. These components have the lowest K_{bw} of the aromatic components examined in this study. Components with greater alkyl substitution or more aromatic rings have larger K_{bw}. Regression analysis of naphthalene log K_{bw}, on degree of alkyl

TABLE 25. PBC Saturated Hydrocarbon Distribution Coefficients

Component	RRT[1]	Oil/Water x 10^3	Log_{10} Oil/Water
C_8	0.2588	700 ± 100	5.85
C_9	0.3528	400 ± 390	5.59
C_{10}	0.4641	400 ± 400	5.61
C_{11}	0.5795	1200 ± 70	6.08
C_{12}	0.6924	1060 ± 20	6.02
C_{13}	0.8006	1500 ± 130	6.17
C_{14}	0.9030	1260 ± 91	6.10
C_{15}	1.0000	1500 ± 130	6.18
C_{16}	1.0917	1400 ± 140	6.14
C_{17}	1.1788	1200 ± 240	6.09
Pristane	1.1789	1100 ± 210	6.05
C_{18}	1.2616	700 ± 170	5.86
Phytane	1.2703	1200 ± 160	6.07
C_{19}	1.3402	1000 ± 150	5.99
C_{20}	1.4152	1200 ± 230	6.07
C_{21}	1.4869	1000 ± 250	6.01
C_{22}	1.5552	900 ± 190	5.93
C_{23}	1.6207	900 ± 220	5.95
C_{24}	1.6840	1200 ± 370	6.08
C_{25}	1.7493	1000 ± 230	5.98
C_{26}	1.8193	1100 ± 150	6.02

[1] Relative retention times with respect to C_{15}.

substitution, gives similar equations for each of the oils except Oxy. SRC II log K_{bw} give the equation $Y = 3.92 + 0.405X$ with $R^2 = 91.0$; PBC K_{bw} give $Y = 3.81 + 0.606X$ with $R^2 = 96.5$; No. 2 fuel oil K_{bw} give $Y = 3.73 + 0.481X$ with $R^2 = 97.7$; and Oxy K_{bw} give $Y = 2.84 + 0.635X$ with $R^2 = 89.6$. These large correlation coefficients show the analytical data is fitted well by the empirical linear equation. Concentrations of aromatic hydrocarbons in a WSF generated from each oil are quite large and are very slightly affected by volatility. Oxy contains lower concentrations of aromatic hydrocarbons and larger concentrations of saturated hydrocarbons than any of the other oils studied. These composition differences might explain why relatively fewer Oxy aromatic hydrocarbons enter the water

TABLE 26. No. 2 Fuel Oil Saturated Hydrocarbon Distribution Coefficients

Component	RRT[1]	Oil/Water x 10^3	Log_{10} Oil/Water
C_8	0.2588	400 ± 120	5.55
C_9	0.3528	400 ± 330	5.63
C_{10}	0.4641	500 ± 300	5.66
C_{11}	0.5795	38 ± 1	4.58
C_{12}	0.6924	260 ± 67	5.42
C_{13}	0.8006	180 ± 82	5.25
C_{14}	0.9030	140 ± 78	5.14
C_{15}	1.0000	130 ± 73	5.10
C_{16}	1.0917	120 ± 70	5.07
C_{17}	1.1788	130 ± 80	5.11
Pristane	1.1789	120 ± 73	5.09
C_{18}	1.2616	140 ± 90	5.15
Phytane	1.2703	140 ± 88	5.15
C_{19}	1.3402	170 ± 93	5.22
C_{20}	1.4152	160 ± 90	5.21
C_{21}	1.4869	170 ± 98	5.23
C_{22}	1.5552	170 ± 44	5.22
C_{23}	1.6207	nd[2]	nd
C_{24}	1.6840	nd	nd
C_{25}	1.7493	nd	nd
C_{26}	1.8193	nd	nd

[1] Relative retention time with respect to C_{15}.
[2] Not determined.

column; they tend to be retained in the oil phase by the nonpolar saturated hydrocarbons. Figure 22 shows a plot of log K_{bw} of SRC II aromatic hydrocarbons against increasing alkyl substitution.

Table 30 contains average K_{ow} values determined for benzenes and naphthalenes determined from a WSF of each of the four oils. Data for benzene components are included, although they are not reliable because of losses of the volatile benzenes in the analytical procedure. Figure 23 shows a graph of log K_{ow} plotted against increasing alkyl substitution for SRC II benzenes and naphthalenes, as well as a plot of literature log K_{ow}

TABLE 27. Total Aromatic Hydrocarbon Concentrations in Oil and Their Corresponding WSF (μg/mL)

Oil Type	Aromatic Hydrocarbon Conc. in Oil	Aromatic Hydrocarbon Conc. in WSF	TOC
SRC II	170000 ± 11000	6.2 ± 0.67	4400 ± 290
Oxy	16000 ± 800	1.9 ± 0.18	310 ± 4
PBC	20000 ± 600	1.3 ± 0.19	26 ± 1
No. 2 Fuel Oil	53000	2.64	120 ± 8

data (21) against alkyl substitution for benzenes. Regression of literature benzene values on alkyl substitution yields the equation $Y = 2.11 + 0.492X$ with $R^2 = 80.7$, indicating some scatter of points about the line. Log K_{ow} data used in the regression analysis of literature data were 2.13 and 2.15 for benzene, 2.69, 2.73, 2.11, and 2.80 for toluene, 3.20, 2.77, 3.15 for the xylenes, and 3.66, 3.66, 3.68, and 3.57 for C_3 benzenes (21). SRC II benzene K_{ow} values subjected to this same regression analysis give the equation $Y = 3.14 + 0.067X$ with an R^2 showing no correlation. However, SRC II K_{ow} data were available for only C_2, C_3, and C_4 benzenes, thus making calculation of a correlation coefficient less meaningful than it would have been if more data points along the X axis had been included. Regression analysis of benzene log K_{ow_2} data for all oils yields the equation $Y = 3.14 + 0.113X$, also with an R^2 value showing no correlation. Aqueous phase concentrations for monocyclic aromatic hydrocarbons were not useful for generating K_{ow} data because of volatility losses during the analytical procedure. Generation of better quality benzene K_{ow} data would require the use of a different analytical procedure for volatile aromatic. Fortunately, data for monocyclic aromatic hydrocarbons are available in the literature.

SRC II naphthalene log K_{ow} data are plotted against increasing alkyl substitution in Figure 23. Regression analysis of SRC II log K_{ow}, on degree of alkyl substitution for naphthalenes, yields the equation $Y = 3.51 + 0.457X$ with $R^2 = 61.7$, showing some scatter of points about the line. However, the trend from a low log K_{ow} for unsubstituted naphthalene to higher values for alkyl substituted naphthalenes is clear. Regressing

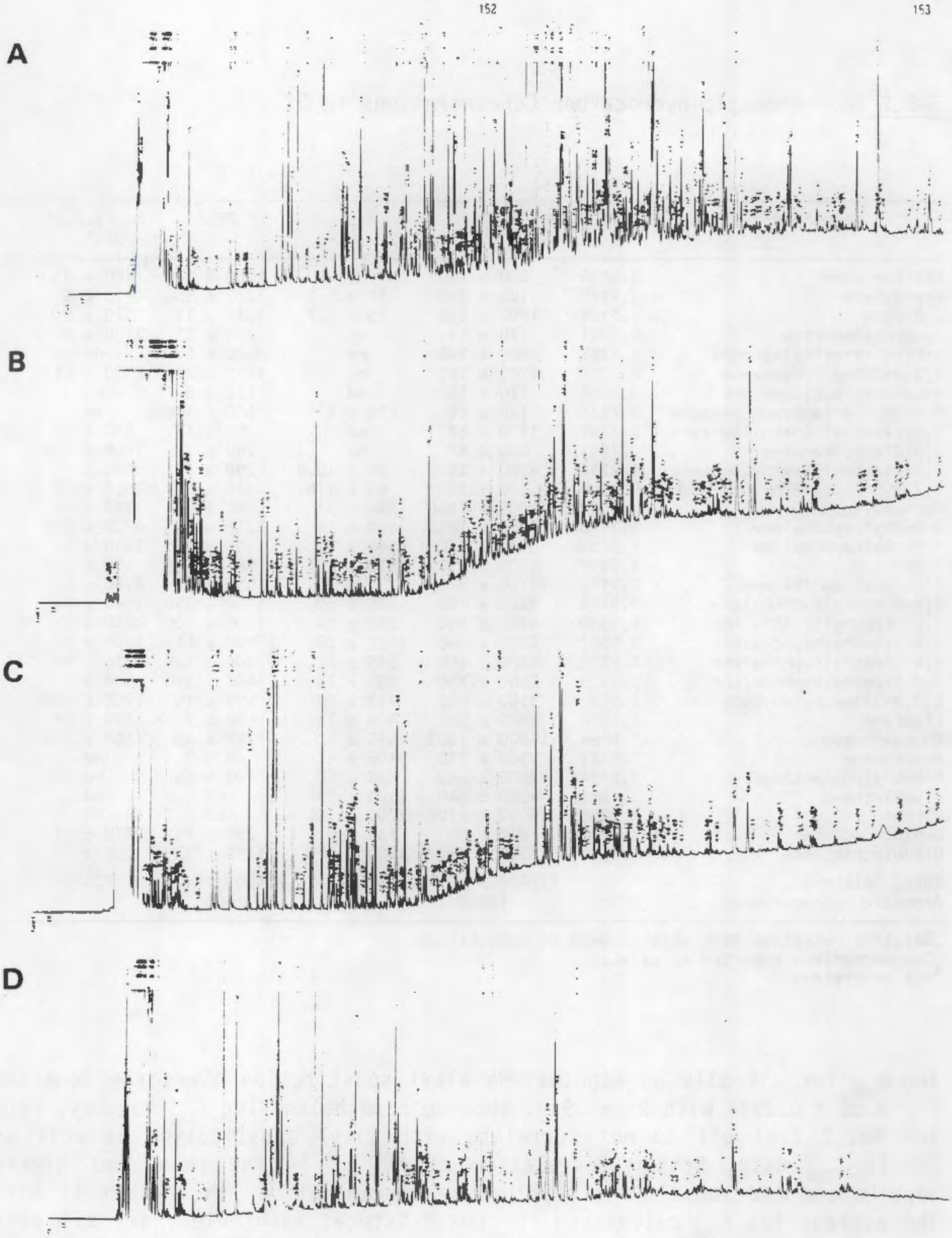

FIGURE 21. Gas Chromatograms of Aromatic Hydrocarbon WSF Extracts (A) SRC II (B) Oxy (C) PBC (D) No. 2 Fuel Oil

TABLE 28. Aromatic Hydrocarbon Concentrations in Oils

Component	RRT[1]	SRC II[2]	Oxy[2]	PBC[2]	No. 2 Fuel Oil[2]
Ethylbenzene	0.4635	600 ± 130	nd[3]	1000 ± 120	280 ± 0
m+p-Xylene	0.4739	1100 ± 230	31 ± 0.9	3200 ± 350	1130 ± 6
o-Xylene	0.5104	1200 ± 210	15 ± 1.7	1230 ± 13	510 ± 9
Isopropylbenzene	0.5581	170 ± 14	nd	250 ± 22	2120 ± 90
1-Ethyl-4-methylbenzene	0.6203	1500 ± 140	nd	390 ± 27	nd
1,2,4-Trimethylbenzene	0.6716	2200 ± 190	nd	1470 ± 78	3990 ± 41
Secondary butylbenzene	0.7005	110 ± 10	nd	180 ± 8	nd
1-Methyl-4-isopropylbenzene	0.7225	120 ± 10	130 ± 6	600 ± 320	nd
1,3-Dimethyl-5-ethylbenzene	0.7787	1170 ± 82	nd	250 ± 13	900 ± 4
1,2-Diethylbenzene	0.7863	650 ± 47	nd	280 ± 11	1800 ± 130
1,2-Dimethyl-5-ethylbenzene	0.8256	4000 ± 290	20 ± 10.8	290 ± 11	2800 ± 32
1,2,3,5-Tetramethylbenzene	0.8853	300 ± 200	60 ± 1.8	320 ± 11	2530 ± 29
Naphthalene	1.0000	18000 ± 1100	560 ± 33	990 ± 76	2730 ± 10
2-Methylnaphthalene	1.1748	29000 ± 1800	450 ± 13	1210 ± 82	6700 ± 38
1-Methylnaphthalene	1.2029	5900 ± 360	480 ± 96	1100 ± 46	3940 ± 9
Biphenyl	1.2999	8900 ± 630	510 ± 48	560 ± 170	300 ± 210
1+2-Ethylnaphthalene	1.3175	28700 ± 970	nd	450 ± 77	2180 ± 1
2,6-Dimethylnaphthalene	1.3388	9200 ± 700	550 ± 50	1100 ± 390	3940 ± 57
1,3-Dimethylnaphthalene	1.3629	4200 ± 350	580 ± 18	1100 ± 120	4230 ± 52
1,7-Dimethylnaphthalene	1.3682	3400 ± 240	1420 ± 28	900 ± 140	2980 ± 50
1,4-Dimethylnaphthalene	1.3778	4700 ± 400	360 ± 12	600 ± 180	2170 ± 95
1,2-Dimethylnaphthalene	1.3919	3300 ± 330	390 ± 11	400 ± 140	680 ± 1
2,3,5-Trimethylnaphthalene	1.5626	3100 ± 400	810 ± 50	490 ± 18	1700 ± 110
Fluorene	1.5930	5400 ± 520	400 ± 23	96 ± 7	750 ± 11
Phenanthrene	1.8464	14000 ± 1300	1470 ± 35	240 ± 15	1500 ± 110
Anthracene	1.8581	2500 ± 270	1100 ± 62	66 ± 5	nd
1-Methylphenanthrene	2.0136	2800 ± 540	650 ± 60	190 ± 10	nd
Fluoranthene	2.1652	4500 ± 540	1300 ± 190	nd	nd
Pyrene	2.2249	6000 ± 1200	2700 ± 780	nd	nd
Benzothiophene	1.0089	970 ± 64	130 ± 9	290 ± 16	2730 ± 13
Dibenzothiophene	1.8434	5900 ± 610	1700 ± 290	1250 ± 37	250 ± 18
Total Selected Aromatic Hydrocarbons		170000 ± 10800	16000 ± 800	20400 ± 600	52000

[1] Relative retention time with respect to naphthalene.
[2] Concentrations reported as µg/mL.
[3] Not determined.

log K_{ow} for all oils on naphthalene alkyl substitution gives the equation $Y = 3.66 + 0.299X$ with $R^2 = 39.9$, showing naphthalene log K_{ow} for Oxy, PBC, and No. 2 fuel oil do not correlate with alkyl substitution as well as SRC II K_{ow} data; better correlation of SRC II is the result of higher naphthalene and substituted naphthalene concentrations in the SRC II WSF. The average log K_{ow} calculated for unsubstituted naphthalene for all oils is 3.61 ± 0.19; this value is higher than the values reported by Leo et al. (21), of 3.37, 3.01, and 3.45 and also higher than the value of 3.14 ± 0.05 determined for single component naphthalene in this study. This difference can be attributed to losses of naphthalene from aqueous phases when

TABLE 29. Average Aromatic Hydrocarbon $\mathrm{Log}_{10}\ K_{bw}$

	SRC II	Oxy	PBC	No. 2 Fuel Oil
C_2 Benzenes	3.87	3.33	3.87	3.59
C_3 Benzenes	4.35	3.33	4.49	4.29
C_4 Benzenes	4.54	3.49	4.66	4.58
Naphthalene	3.90	2.91	3.87	3.67
C_1 Naphthalenes	4.35	3.42	4.32	4.23
C_2 Naphthalenes	4.70	4.12	5.06	4.71
C_3 Naphthalenes	4.84	4.77	5.55	5.09
Phenanthrene+ Anthracene	5.00	4.54	5.28	4.89
C_1 Phenanthrene	5.25	4.94	5.32	nd
Fluoranthene	5.19	5.62	nd[1]	nd
Pyrene	5.10	5.53	nd	nd
Benzothiophene	4.18	3.09	4.81	3.95
Dibenzothiophene	4.73	4.10	5.02	4.77

[1] Not determined.

naphthalene concentrations are very low, through volatilization and teflon and glass surface adsorption during analysis. At the high naphthalene concentrations used in single, standard component K_{ow} determination, losses due to volatilization and surface adsorption become relatively less important. Literature log K_{ow} for alkyl substituted naphthalenes are not available for comparisons with data generated in this study.

Detailed tabulations of K_{bw} and K_{ow} are found in Tables 31-34 for individual aromatic components in each oil.

HETEROCYCLIC SULFUR COMPOUNDS

Concentrations in oil, octanol, and aqueous phases of the two heterocyclic sulfur components studied, benzothiophene and dibenzothiophene, are shown in Tables 12A through 15A in the Appendix, along with the aromatic hydrocarbon data. Both benzothiophene and dibenzothiophene are found in all oils studied.

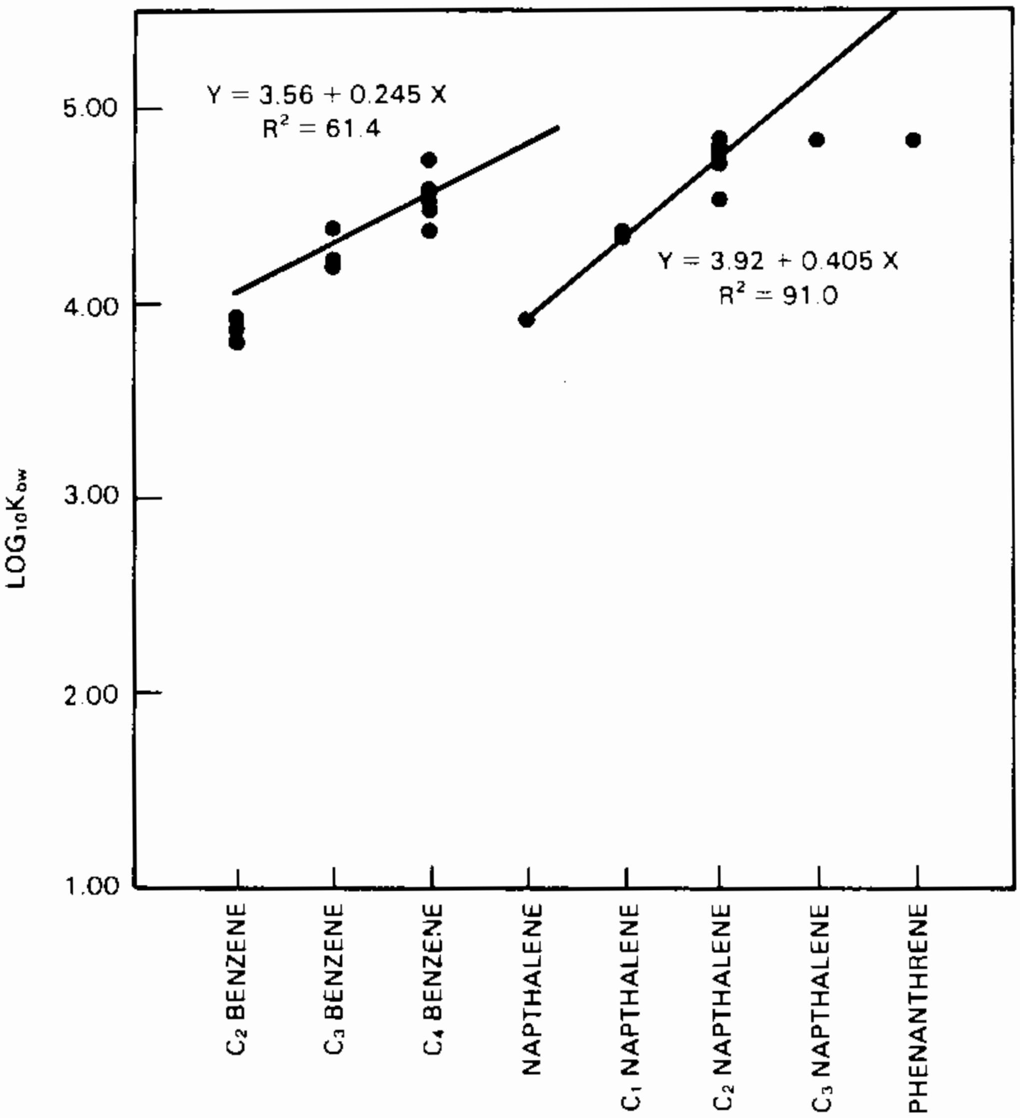

FIGURE 22. SRC II Aromatic Hydrocarbon Log_{10} K_{bw} Plotted Against Increasing Alkyl Substitution. [C_3 naphthalene aqueous phase concentration was very low, thus the distribution coefficient was not reliable and was not used in the regression analysis.]

TABLE 30. Average Aromatic Hydrocarbon $\mathrm{Log}_{10}\ K_{ow}$

	SRC II	Oxy	PBC	No. 2 Fuel Oil
C_2 Benzenes	3.50	2.67	3.90	3.22
C_3 Benzenes	3.70	3.61	3.66	2.78
C_4 Benzenes	3.66	nd	3.57	3.53
Naphthalene	3.50	3.80	3.73	3.39
C_1 Naphthalenes	3.98	4.17	4.06	3.82
C_2 Naphthalenes	4.42	4.13	4.56	3.94
C_3 Naphthalenes	nd[1]	nd	nd	nd
Phenanthrene+ Anthracene	nd	3.50	nd	nd
C_1 Phenanthrene	nd	nd	nd	nd
Fluoranthene	nd	nd	nd	nd
Pyrene	nd	nd	nd	nd
Benzothiophene	3.35	3.32	3.63	3.14
Dibenzothiophene	nd	2.90	2.92	nd

[1] Not determined.

Partition coefficients for these components are found in Tables 31-34 with aromatic hydrocarbon data. The log K_{bw} determined for benzothiophene range from a low of 3.09 for Oxy to a high of 4.81 for PBC, while those of dibenzothiophene range from 4.10 for Oxy to 5.02 for PBC. These values are similar to K_{bw} for aromatic hydrocarbons of similar molecular weight. Calculated log K_{ow} for benzothiophene vary only very slightly among the oils studied, yielding an average value of 3.30 ± 0.13, a figure slightly higher than published literature values of 3.09 and 3.12 (21). Concentrations of dibenzothiophene in samples were too low to permit accurate calculation of log K_{ow} values.

CARBOXYLIC ACIDS

All four oils studied contained some acids; however, concentrations varied widely between the different source oils. Some acids were detected in PBC but concentrations were too low to quantitate. Concentrations of selected acids in three of the four oils are shown in Table 35. Concentrations of selected acids in oil and aqueous phases are found in

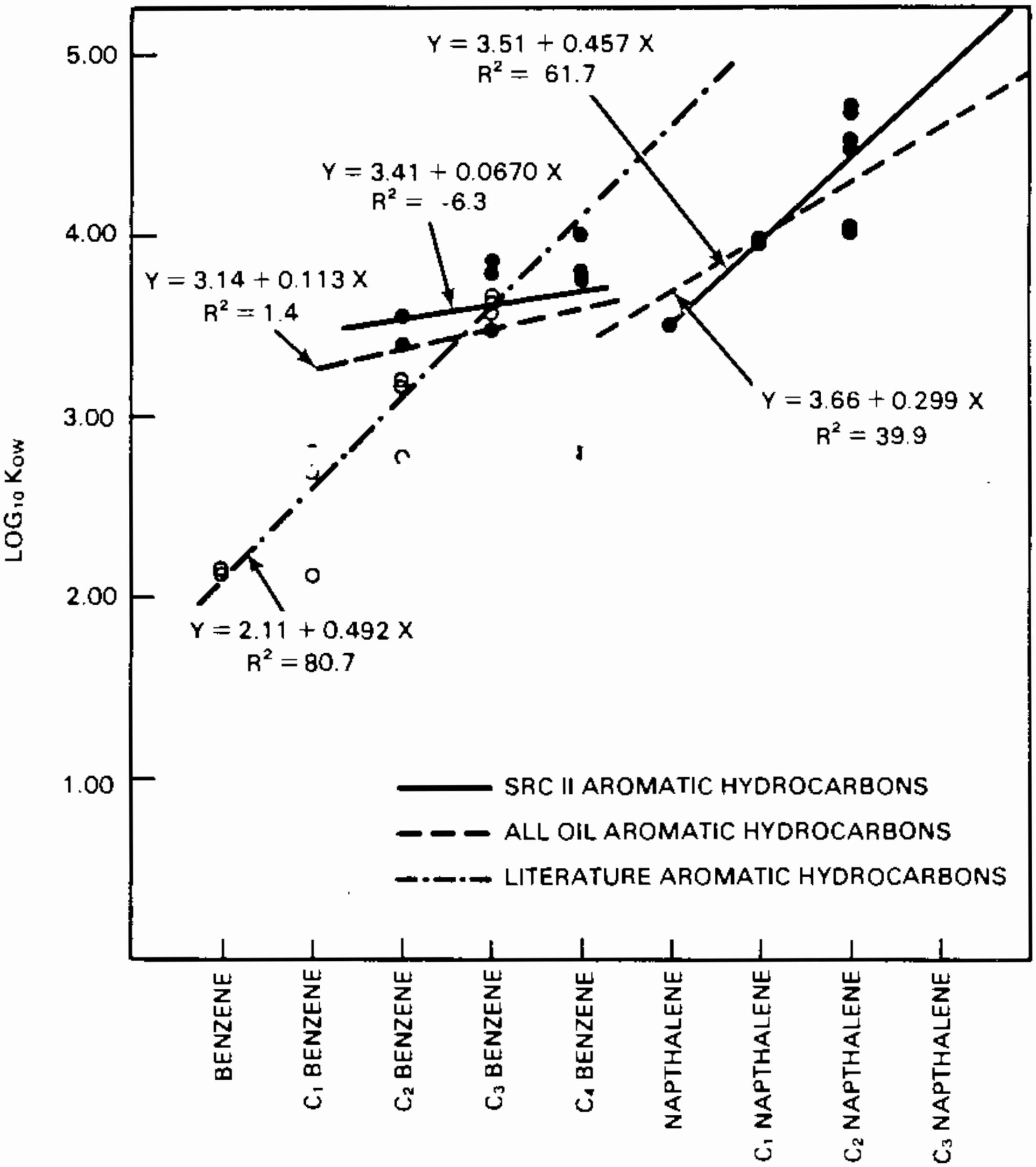

FIGURE 23. SRC II Aromatic Hydrocarbon Log_{10} K_{ow} Plotted Against Increasing Alkyl Substitution. [Literature K_{ow} values, shown by hollow circles, are plotted on the graph and a line shows the results of linear regression analysis of these data.]

TABLE 31. SRC II Aromatic Hydrocarbon Distribution Coefficients

Component	RRT[1]	Oil/Water X 10^3	Log$_{10}$ Oil/Water	Octanol/Water X 10^3	Log$_{10}$ Octanol/Water	Literature Octanol/Water[2]
Ethylbenzene	0.4635	8 ± 1.4	3.89	2.5 ± 1.1	3.40	3.15
m+p-Xylene	0.4739	8 ± 1.4	3.91	3.5 ± 1.5	3.55	3.20, 3.15
o-Xylene	0.5104	7 ± 1.3	3.81	3.5 ± 1.7	3.55	2.77
Isopropylbenzene	0.5581	25 ± 5.9	4.39	7.2 ± 1.7	3.86	3.66
1-Ethyl-4-methylbenzene	0.6203	16 ± 6.7	4.19	2.9 ± 0.6	3.46	
1,2,4-Trimethylbenzene	0.6716	16 ± 3.4	4.21	6.1 ± 2.5	3.79	
Secondary butylbenzene	0.7005	39 ± 4.2	4.59	0.6 ± 0.1	2.80	
1-Methyl-4-isopropylbenzene	0.7225	36 ± 8.4	4.56	6.3 ± 5.9	3.80	
1,3-Dimethyl-5-ethylbenzene	0.7787	50 ± 25	4.74	5.9 ± 5.1	3.77	
1,2-Diethylbenzene	0.7863	34 ± 6.5	4.54	5.8 ± 2.1	3.76	
1,2-Dimethyl-5-ethylbenzene	0.8256	23 ± 4.5	4.36	6.3 ± 2.7	3.80	
1,2,3,5-Tetramethylbenzene	0.8853	30 ± 6.2	4.48	10.3 ± 4.1	4.01	
Naphthalene	1.0000	8 ± 1.0	3.90	3.1 ± 0.6	3.50	3.45, 3.37, 3.01
2-Methylnaphthalene	1.1748	23 ± 2.3	4.36	9.7 ± 2.1	3.99	
1-Methylnaphthalene	1.2029	22 ± 2.0	4.34	9.4 ± 1.7	3.97	
Biphenyl	1.2999	33 ± 2.3	4.52	13.3 ± 3.1	4.12	4.04, 4.09, 3.16
1+2-Ethylnaphthalene	1.3175	35 ± 2.4	4.54	11.6 ± 2.6	4.06	
2,6-Dimethylnaphthalene	1.3388	52 ± 4.0	4.71	35.5 ± 12.4	4.55	
1,3-Dimethylnaphthalene	1.3629	52 ± 4.0	4.72	11.2 ± 4.9	4.05	
1,7-Dimethylnaphthalene	1.3682	70 ± 17	4.81	30.3 ± 14.0	4.48	
1,4-Dimethylnaphthalene	1.3778	55 ± 4.0	4.74	48.6 ± 20.4	4.69	
1,2-Dimethylnaphthalene	1.3919	70 ± 12	4.85	52.3 ± 56.3	4.71	
2,3,5-Trimethylnaphthalene	1.5626	70 ± 7.4	4.84	nd[3]	nd	
Fluorene	1.5930	48 ± 2.3	4.68	28.2 ± 8.4	4.44	4.46
Phenanthrene	1.8464	67 ± 4.9	4.83	nd	nd	4.45
Anthracene	1.8581	150 ± 28	5.17	nd	nd	
1-Methylphenanthrene	2.0136	180 ± 45	5.25	nd	nd	
Fluoranthene	2.1652	150 ± 13	5.19	nd	nd	
Pyrene	2.2249	130 ± 23	5.10	nd	nd	
Benzothiophene	1.0089	15 ± 1.7	4.18	2.3 ± 0.4	3.35	3.09, 3.12
Dibenzothiophene	1.8434	54 ± 6.3	4.73	nd	nd	

[1] Relative retention times with respect to naphthalene.
[2] Reference 21.
[3] Not determined.

TABLE 32. Oxy Aromatic Hydrocarbon Distribution Coefficients

Component	RRT[1]	Oil/Water X 10^3	Log_{10} Oil/Water	Octanol/Water X 10^3	Log_{10} Octanol/Water	Literature Octanol/Water[2]
Ethylbenzene	0.4635	nd[3]	nd	nd	nd	3.15
m+p-Xylene	0.4739	2.8 ± 0.5	3.45	0.39 ± 0.93	2.59	3.20, 3.15
o-Xylene	0.5104	1.6 ± 0.8	3.21	0.56 ± 1.0	2.75	2.77
Isopropylbenzene	0.5581	nd	nd	nd	nd	3.66
1-Ethyl-4-methylbenzene	0.6203	nd	nd	nd	nd	
1,2,4-Trimethylbenzene	0.6716	2.2 ± 0.3	3.33	4.1 ± 9.5	3.61	
Secondary butylbenzene	0.7005	nd	nd	nd	nd	
1-Methyl-4-isopropylbenzene	0.7225	1.7 ± 0.2	3.23	nd	nd	
1,3-Dimethyl-5-ethylbenzene	0.7787	nd	nd	nd	nd	
1,2-Diethylbenzene	0.7863	nd	nd	nd	nd	
1,2-Dimethyl-5-ethylbenzene	0.8256	4.2 ± 0.6	3.62	nd	nd	
1,2,3,5-Tetramethylbenzene	0.8853	4.2 ± 0.4	3.63	nd	nd	
Naphthalene	1.0000	0.8 ± 0.1	2.91	6.2 ± 4.5	3.80	3.37, 3.01, 3.45
2-Methylnaphthalene	1.1748	2.5 ± 0.4	3.40	14.1 ± 7.0	4.15	
1-Methylnaphthalene	1.2029	2.7 ± 0.4	3.44	15.7 ± 14.3	4.19	
Biphenyl	1.2999	4.0 ± 0.3	3.60	8.3 ± 2.2	3.92	4.09, 3.16, 4.04
1+2-Ethylnaphthalene	1.3175	nd	nd	nd	nd	
2,6-Dimethylnaphthalene	1.3388	9.5 ± 0.8	3.98	nd	nd	
1,3-Dimethylnaphthalene	1.3629	9.1 ± 0.7	3.96	nd	nd	
1,7-Dimethylnaphthalene	1.3682	9.0 ± 0.9	3.95	21.4 ± 13.3	4.33	
1,4-Dimethylnaphthalene	1.3778	32 ± 8.5	4.51	nd	nd	
1,2-Dimethylnaphthalene	1.3919	15 ± 1.7	4.18	nd	nd	
2,3,5-Trimethylnaphthalene	1.5626	59 ± 3.7	4.77	nd	nd	
Fluorene	1.5930	7.2 ± 0.7	3.86	nd	nd	
Phenanthrene	1.8464	20.0 ± 1.8	4.30	5.1 ± 8.0	3.70	4.46
Anthracene	1.8581	60 ± 5.4	4.78	2.0 ± 3.9	3.31	4.45
1-Methylphenanthrene	2.0136	88 ± 17	4.94	nd	nd	
Fluoranthene	2.1652	42 ± 56	5.62	nd	nd	
Pyrene	2.2249	340 ± 68	5.53	nd	nd	
Benzothiophene	1.0089	1.2 ± 0.1	3.09	2.1 ± 0.9	3.32	3.09, 3.12
Dibenzothiophene	1.8434	2.5 ± 0.4	3.40	0.8 ± 1.2	2.90	

[1] Relative retention times with respect to naphthalene.
[2] Reference 21.
[3] Not determined.

TABLE 33. PBC Aromatic Hydrocarbon Distribution Coefficients

Component	RRT[1]	Oil/Water X 10^3	Log_{10} Oil/Water	Octanol/Water X 10^3	Log_{10} Octanol/Water	Literature Octanol/Water[2]
Ethylbenzene	0.4635	8.6 ± 0.8	3.93	7.3 ± 2.0	3.86	3.15
m+p-Xylene	0.4739	8.0 ± 1.1	3.91	9.9 ± 2.5	4.00	3.20, 3.15
o-Xylene	0.5104	5.8 ± 1.1	3.76	6.8 ± 1.8	3.83	2.77
Isopropylbenzene	0.5581	22 ± 2.0	4.34	nd	nd	3.66
1-Ethyl-4-methylbenzene	0.6203	27 ± 2.8	4.42	1.3 ± 0.3	3.12	
1,2,4-Trimethylbenzene	0.6716	18 ± 3.3	4.25	16 ± 4.3	4.20	
Secondary butylbenzene	0.7005	90 ± 27	4.94	1.8 ± 1.6	3.25	
1-Methyl-4-isopropylbenzene	0.7225	16 ± 3.0	4.19	7.7 ± 2.4	3.89	
1,3-Dimethyl-5-ethylbenzene	0.7787	68 ± 6.5	4.83	nd	nd	
1,2-Diethylbenzene	0.7863	55 ± 6.1	4.74	nd	nd	
1,2-Dimethyl-5-ethylbenzene	0.8256	61 ± 7.8	4.79	nd	nd	
1,2,3,5-Tetramethylbenzene	0.8853	60 ± 11	4.76	nd	nd	
Naphthalene	1.0000	7.4 ± 1.2	3.87	5.4 ± 0.9	3.73	3.37, 3.01, 3.45
2-Methylnaphthalene	1.1748	22 ± 3.5	4.33	11.4 ± 2.7	4.06	
1-Methylnaphthalene	1.2029	20 ± 2.8	4.31	11.6 ± 1.8	4.06	
Biphenyl	1.2999	57 ± 13	4.76	nd	nd	4.09, 3.16, 4.04
1+2-Ethylnaphthalene	1.3175	130 ± 28	5.11	nd	nd	
2,6-Dimethylnaphthalene	1.3388	120 ± 31	5.08	nd	nd	
1,3-Dimethylnaphthalene	1.3629	88 ± 29	4.95	36.2 ± 30.7	4.56	
1,7-Dimethylnaphthalene	1.3682	96 ± 21	4.98	nd	nd	
1,4-Dimethylnaphthalene	1.3778	120 ± 36	5.08	nd	nd	
1,2-Dimethylnaphthalene	1.3919	150 ± 47	5.17	nd	nd	
2,3,5-Trimethylnaphthalene	1.5626	360 ± 41	5.55	nd	nd	
Fluorene	1.5930	520 ± 25	4.72	nd	nd	
Phenanthrene	1.8464	76 ± 17	4.89	3.0 ± 1.1	3.47	4.46
Anthracene	1.8581	46 ± 25	5.66	nd	nd	4.45
1-Methylphenanthrene	2.0136	210 ± 30	5.32	nd	nd	
Fluoranthene	2.1652	nd[3]	nd	nd	nd	
Pyrene	2.2249	nd	nd	nd	nd	
Benzothiophene	1.0089	65 ± 14	4.81	4.3 ± 3.7	3.63	3.09, 3.12
Dibenzothiophene	1.8434	110 ± 37	5.02	0.8 ± 0.3	2.92	

[1] Relative retention times with respect to naphthalene.
[2] Reference 21.
[3] Not determined.

TABLE 34. No. 2. Fuel Aromatic Hydrocarbon Distribution Coefficients

Component	RRT[1]	Oil/Water X 10^3	Log$_{10}$ Oil/Water	Octanol/Water X 10^3	Log$_{10}$ Octanol/Water	Literature Octanol/Water[2]
Ethylbenzene	0.4635	3.4 ± 0.6	3.53	1.5 ± 0.7	3.17	3.15
m+p-Xylene	0.4739	4.7 ± 0.6	3.67	2.1 ± 0.7	3.32	3.20, 3.15
o-Xylene	0.5104	3.7 ± 0.4	3.56	1.4 ± 0.3	3.16	2.77
Isopropylbenzene	0.5581	27 ± 8.1	4.44	0.2 ± 0.0	2.30	3.66
1-Ethyl-4-methylbenzene	0.6203	nd[3]	nd	nd	nd	
1,2,4-Trimethylbenzene	0.6716	14 ± 1.6	4.14	1.8 ± 0.3	3.25	
Secondary butylbenzene	0.7005	nd	nd	nd	nd	
1-Methyl-4-isopropylbenzene	0.7225	36 ± 9.4	4.56	nd	nd	
1,3-Dimethyl-5-ethylbenzene	0.7787	55 ± 6.5	4.74	2.0 ± 0.8	3.30	
1,2-Diethylbenzene	0.7863	42 ± 5.3	4.62	nd	nd	
1,2-Dimethyl-5-ethylbenzene	0.8256	29 ± 4.2	4.46	3.8 ± 1.2	3.58	
1,2,3,5-Tetramethylbenzene	0.8853	34 ± 5.2	4.53	5.1 ± 1.1	3.71	
Naphthalene	1.0000	4.7 ± 0.6	3.67	2.5 ± 0.1	3.39	3.37, 3.01, 3.45
2-Methylnaphthalene	1.1748	17 ± 2.8	4.23	6.8 ± 1.2	3.83	
1-Methylnaphthalene	1.2029	17 ± 2.6	4.23	6.4 ± 0.8	3.81	
Biphenyl	1.2999	38 ± 5.2	4.57	22.9 ± 2.8	4.36	4.09, 3.16, 4.04
1+2-Ethylnaphthalene	1.3175	60 ± 12.6	4.78	nd	nd	
2,6-Dimethylnaphthalene	1.3388	56 ± 14.4	4.74	nd	nd	
1,3-Dimethylnaphthalene	1.3629	44 ± 7.8	4.64	15.3 ± 4.0	4.18	
1,7-Dimethylnaphthalene	1.3682	54 ± 11.3	4.73	10.6 ± 1.3	4.02	
1,4-Dimethylnaphthalene	1.3778	53 ± 10.1	4.73	4.0 ± 0.4	3.60	
1,2-Dimethylnaphthalene	1.3919	44 ± 9.5	4.64	9.1 ± 2.1	3.96	
2,3,5-Trimethylnaphthalene	1.5626	120 ± 52	5.09	nd	nd	
Fluorene	1.5930	92 ± 38	4.96	nd	nd	
Phenanthrene	1.8464	78 ± 20	4.89	nd	nd	4.46
Anthracene	1.8581	nd	nd	nd	nd	4.45
1-Methylphenanthrene	2.0136	nd	nd	nd	nd	
Fluoranthene	2.1652	nd	nd	nd	nd	
Pyrene	2.2249	nd	nd	nd	nd	
Benzothiophene	1.0089	8.9 ± 1.1	3.95	1.4 ± 0.1	3.14	3.09, 3.12
Dibenzothiophene	1.8434	59 ± 14	4.77	nd	nd	

[1] Relative retention times with respect to naphthalene.
[2] Reference 21.
[3] Not determined.

TABLE 35. Carboxylic Acid Concentrations in Oils

Component	RRT[1]	SRC II[2]	Oxy[2]	No. 2 Fuel Oil[2]
Hexanoic acid	0.4611	12 ± 0.2	27 ± 2.3	nd
C_6 Acid	0.6215	0.9 ± 0.27	nd	nd
C_6 Acid	0.6953	1.9 ± 0.20	nd	nd
Heptanoic acid	0.7161	4.0 ± 0.08	24 ± 5.6	0.42 ± 0.10
C_7 Acid	0.7666	0.7 ± 0.02	nd	nd
C_7 Acid	0.7955	10 ± 1.4	nd	nd
Benzoic acid	0.9131	4 ± 1.2	nd	1.3 ± 0.10
Octanoic acid	1.0000	2.5 ± 0.08	80 ± 20	0.61 ± 0.13
C_8 Acid	1.1195	36 ± 2.2	nd	nd
C_1 Benzoic acid	1.1957	30 ± 3.3	nd	nd
Nonanoic acid	1.2903	2.0 ± 0.32	140 ± 32	0.75 ± 0.13
C_9 Acid	1.3023	6.6 ± 0.64	nd	nd
C_9 Acid	1.4090	1.1 ± 0.03	nd	nd
C_9 Acid	1.4451	2.6 ± 0.16	nd	nd
C_2 Benzoic acid	1.4924	1.1 ± 0.16	nd	nd
Decanoic acid	1.5750	1.5 ± 0.05	220 ± 27	0.73 ± 0.16
Undecanoic acid	1.8476	nd[3]	64 ± 7.6	nd
Total Selected Carboxylic Acids		120 ± 6	420 ± 28	3.8 ± 0.43

[1] Relative retention times with respect to octanoic acid - methyl ester.
[2] Concentrations reported as µg/mL.
[3] Not determined.

Tables 16A through 18A in the Appendix. Flame ionization chromatograms of a WSF generated from each oil source oil are shown in Figure 24. The chromatogram of PBC acid methyl esters indicates the presence of some acids, but this sample required concentration to less than 200 µL before any FID peaks could be detected. This sample concentration caused interference peaks to dominate the chromatographic pattern. Mass spectral monitoring of a PBC-derivatized acid extract revealed the presence of a few aliphatic acids, but concentrations were too low for single ion peaks to be correlated with FID peaks for quantifitation. SRC II contained the widest variety of carboxylic acid species, although concentrations of individual components were low, ranging from about 12.4 µg/mL for hexanoic acid to 1.5 µg/mL for decanoic acid in the parent oil. Mass spectral analysis of an SRC II WSF revealed the presence of a large number of branched aliphatic acids, in addition to the straight chain homologous series. Additionally, benzoic acid and several alkyl substituted benzoic acids were present.

Oxy contained relatively large amounts of straight chain aliphatic acids, from hexanoic acid through undecanoic acid. Mass spectral analysis of a WSF indicated nearly all the acid fraction consisted of this homologous series of normal aliphatic acids.

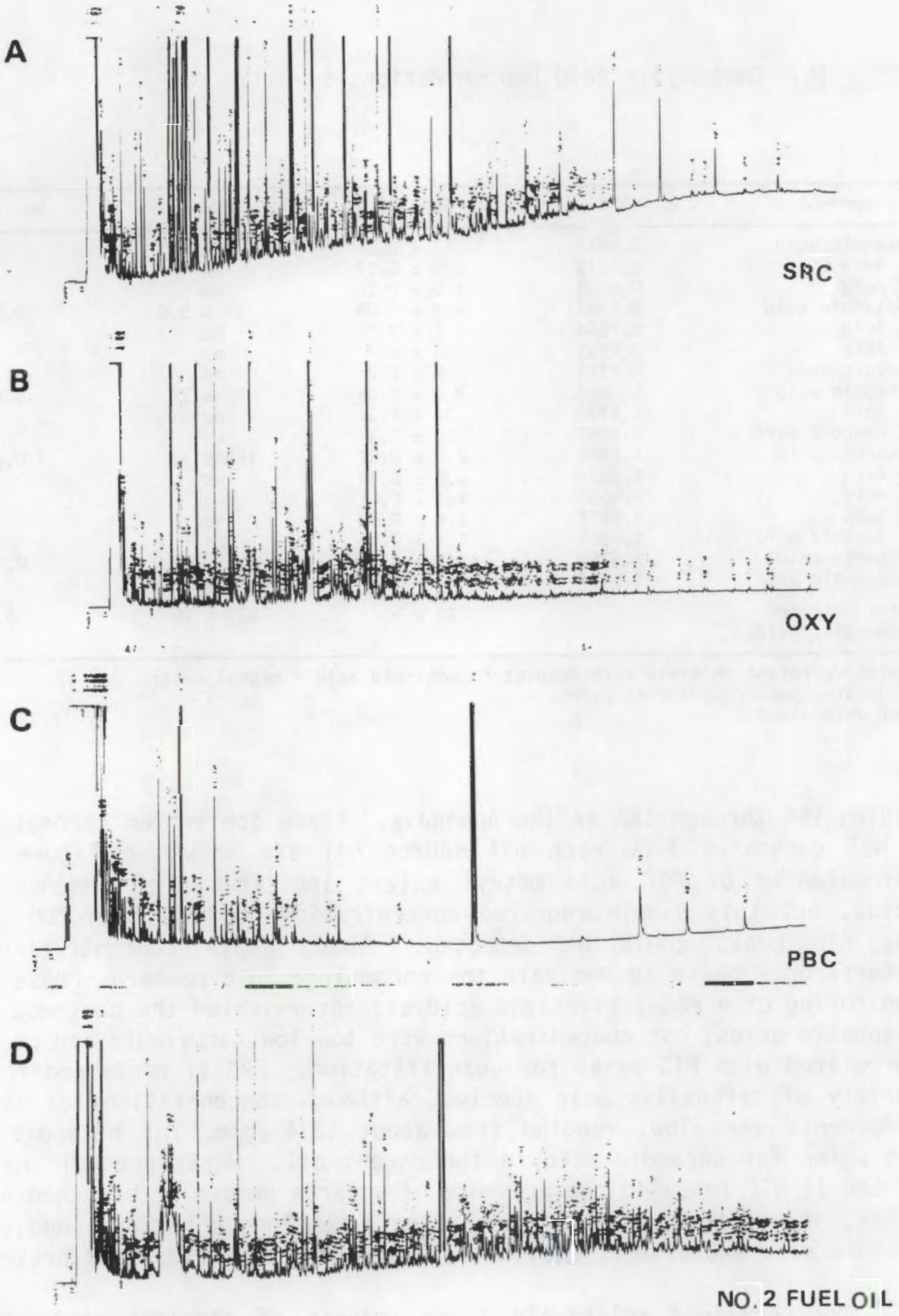

FIGURE 24. Gas Chromatograms of Acid WSF Extracts
(A) SRC II (B) Oxy (C) PBC (D) No. 2 Fuel Oil

Acids found in No. 2 fuel oil fell within the fairly narrow range from heptanoic acid through decanoic acid. Mass spectral analysis revealed the presence of some branched aliphatic acids, as well as some aromatic acids. Benzoic acid was present in levels high enough to be quantified by FID but substituted benzoic acids were not.

Distribution data for these acids are tabulated in Tables 36 through 38. Linear regression equations were calculated correlating log K_{bw} with carbon chain length for normal aliphatic carboxylic acids from heptanoic through decanoic acids in the three oils for which data was obtained. Each regression yielded a negative intercept, -1.39 for SRC II, -3.93 for Oxy, and -0.572 for No. 2 fuel oil. Figure 25 shows the log K_{bw} for Oxy carboxylic acids plotted against increasing carbon chain length for heptanoic acid through undecanoic acid. The measured log K_{bw} for hexanoic acid, for each oil, is considerably higher than the value calculated from the regression equations. This difference shows that the water phase concentrations relative to the oil phase concentrations are lower for hexanoic acid than for heptanoic acid and is possibly the result of ionization in the water phase and dimerization of the acids in the oil phases (21). Other components present in the samples could cause an abrupt

TABLE 36. SRC II Acid Distribution Coefficients

Component	RRT[1]	Oil Water	$\log_{10}$ Oil/Water	Octanol/Water	$\log_{10}$ Octanol/Water	Literature Octanol/Water[2]
Hexanoic acid	0.4611	8.3 ± 1.92	0.92	15 ± 2.4	1.18	1.88, 1.92
C_6 Acid	0.6215	17 ± 2.6	1.23	240 ± 82	2.37	
C_6 Acid	0.6953	15 ± 2.5	1.17	120 ± 90	2.07	
Heptanoic acid	0.7161	4.7 ± 1.29	0.67	7.0 ± 1.1	0.84	
C_7 Acid	0.7666	5.1 ± 2.29	0.71	4.6 ± 0.81	0.66	
C_7 Acid	0.7955	80 ± 11.8	1.90	450 ± 37	2.65	
Benzoic acid	0.9131	5.5 ± 1.91	0.74	10.1 ± 1.9	1.01	1.87
Octanoic acid	1.0000	17 ± 3.6	1.22	18 ± 5.1	1.25	
C_8 Acid	1.1195	140 ± 41	2.16	650 ± 91	2.81	
C_1 Benzoic acid	1.1957	78 ± 23.4	1.89	310 ± 78	2.49	
Nonanoic acid	1.2903	23 ± 5.8	1.36	86 ± 14	1.93	
C_9 Acid	1.3023	82 ± 36.1	1.92	570 ± 144	2.76	
C_9 Acid	1.4090	16 ± 8.9	1.20	44 ± 2.4	1.64	
C_9 Acid	1.4451	76 ± 27.2	1.88	nd[3]	nd	
C_2 Benzoic acid	1.4924	13 ± 6.1	1.11	nd	nd	
Decanoic acid	1.5750	45 ± 13.9	1.65	nd	nd	

[1] Relative retention times with respect to octanoic acid - methylester.
[2] Reference 21.
[3] Not determined.

TABLE 37. Oxy Acid Distribution Coefficients

Component	RRT[1]	Oil Water	Log_{10} Oil/Water	Octanol/Water	Log_{10} Octanol/Water	Literature Octanol/Water[2]
Hexanoic acid	0.4611	44 ± 11	1.64	94 ± 19	1.97	1.88, 1.92
Heptanoic acid	0.7161	1.1 ± 0.22	0.03	4.0 ± 0.50	0.60	
Octanoic acid	1.0000	2.6 ± 0.29	0.41	13 ± 0.9	1.12	
Nonanoic acid	1.2903	10 ± 1.4	1.00	65 ± 10.6	1.81	
Decanoic acid	1.5750	49 ± 0.5	1.69	370 ± 94	2.57	
Undecanoic acid	1.8476	140 ± 22	2.16	770 ± 160	2.89	

[1] Relative retention times with respect to octanoic acid - methylester.
[2] Reference 21.

TABLE 38. No. 2 Fuel Oil Acid Distribution Coefficients

Component	RRT[1]	Oil Water	Log_{10} Oil/Water	Octanol/Water	Log_{10} Octanol/Water	Literature Octanol/Water[2]
Heptanoic acid	0.4611	6.6 ± 0.38	0.82	34.0	1.53	
Benzoic acid	0.9131	18 ± 3.3	1.25	61	1.78	1.87
Octanoic acid	1.0000	14 ± 1.3	1.14	76	1.88	
Nonanoic acid	1.2903	23 ± 2.2	1.35	135	2.13	
C_9 Acid	1.3023	13 ± 3.5	1.12	69	1.84	
Decanoic acid	1.5750	27 ± 7.9	1.44	210	2.33	

[1] Relative retention times with respect to octanoic acid - methylester.
[2] Reference 21.

discontinuity in the linear trend of oil/water distribution of acids between hexanoic and heptanoic acids.

Figure 26 shows log K_{ow} plotted against increasing alkyl carbon chain length for Oxy aliphatic acids. The log K_{ow} determined for Oxy hexanoic acid in this study was 1.97, which is very close to the literature values of 1.88 and 1.92 (21) and close to the log K_{ow} determined in this study for hexanoic acid of 1.70 in the single component system. However, this hexanoic acid point falls very far from the empirical line correlating log K_{ow} with alkyl carbon number for the higher molecular weight aliphatic acids. Oxy acids from heptanoic acid through undecanoic acid show a straight line correlation between alkyl carbon chain length and log K_{ow}, yielding a regression line $Y = -3.63 + 0.603X$ with $R^2 = 98.3$. As with the

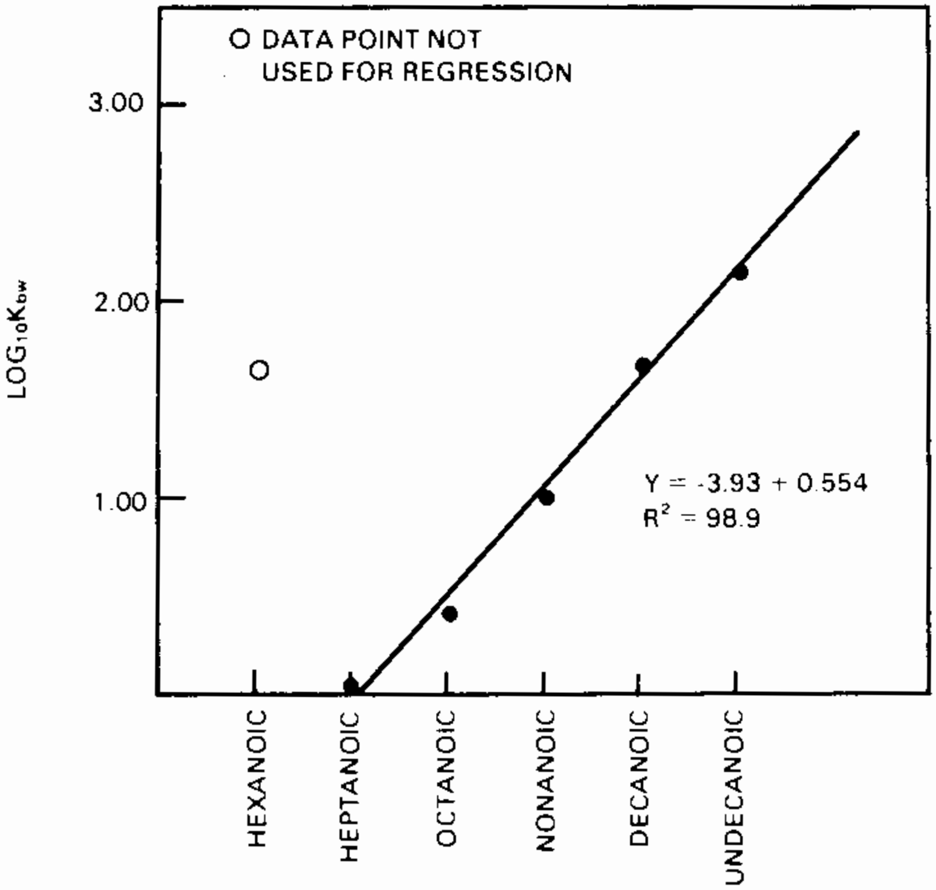

FIGURE 25. Oxy Carboxylic Acid Log_{10} K_{bw} Plotted Against Increasing Carbon Chain Length. [The distribution coefficient for hexanoic acid shows a deviation from linearity and was not included in the linear regression analysis.]

log K_{bw}, log K_{ow} for hexanoic acid is higher than log K_{ow} for heptanoic acid, probably the result of ionization in the water phase and dimerization in the octanol phase or of some interaction of other sample components with the measurement of carboxylic acid K_{ow}. Unfortunately, no literature K_{ow} data could be located for normal aliphatic acids of more than six carbons in length for comparison with data generated in this study. Examination of

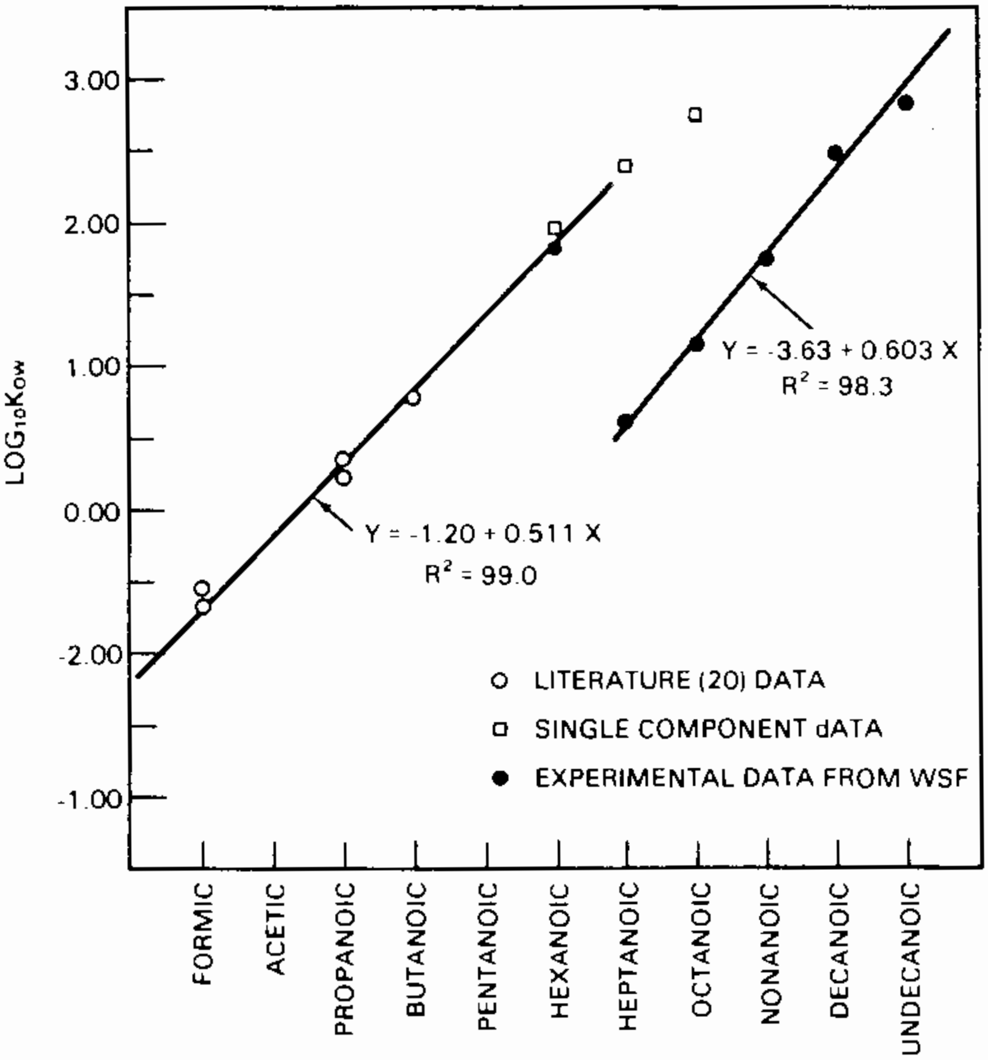

FIGURE 26. Oxy Carboxylic Acid Log_{10} K_{ow} Plotted Against Increasing Carbon Chain Length. [The K_{ow} value for hexanoic acid shows a deviation from linearity and was not included in the regression analysis.]

literature data (21) for log K_{ow}, for normal carboxylic acids of less than six carbon atoms, shows a steady decrease in log K_{ow} with decreasing carbon chain length. Both heptanoic and octanoic acid K_{ow} data were determined for single component systems in an attempt to determine whether the discontinuity in Figure 26 is caused by the presence of other sample components or by ionization and dimerization of the acids in the aqueous phase. Replicate K_{ow} determinations yielded an average log K_{ow} of 2.39 for heptanoic acid and 2.74 for octanoic acid. These data points fall very close to the regression line determined from use of literature K_{ow} data for linear acids of six or fewer carbon atoms, indicating that other components present in the sample are responsible for the discontinuity. Campbell et al. (15) found that the presence of phenol in an equilibrium system of pyridine, water, and toluene increases the calculated distribution coefficient by increasing the solvent phase pyridine concentration. A similar interaction is probably occurring between acids and nitrogen bases in this study.

CONCLUSIONS

Many organic chemical constituents have been identified and quantified in representative petroleum and synthetic fuel oils. Total concentrations of components quantified in each of the compound classes are summarized in Table 39. These data show that chemical composition varies among the four oils. Clearly, SRC II is the most aromatic of any of the oils studied; nearly half of SRC II can be accounted for by components containing an aromatic ring. Of the total aromatic components in SRC II, nearly half are water-extractable phenols.

Oil/water and octanol/water distribution coefficients were determined for a wide variety of components known to be present in natural and synthetically-derived oils, providing data useful to computer modelers studying the fate of oil spills in the aquatic environment. More importantly, it was demonstrated that multiple, accurate K_{ow} data may be determined by equilibrating a complex aqueous solution with octanol, determining concentrations of components in both resultant phases, and calculating experimental K_{ow} data from this information. Only carboxylic acid K_{bw} and K_{ow} data were affected by the presence of other components in the sample.

TABLE 39. Total Concentrations of Components Classes Quantitated in Four Oils

	Oil Concentration in µg/mL			
Component Class	SRC II	Oxy	PBC	No. 2 Fuel Oil
Phenols	270,000	4,000	90	430
Nitrogen bases	20,000	1,200	trace	100
Saturated hydrocarbons	17,000	84,000	55,000	140,000
Aromatic hydrocarbons	170,000	14,000	19,000	50,000
Benzothiophene	970	130	290	2,700
Dibenzothiophene	5,900	1,700	1,300	250
Carboxylic acids	120	420	trace	4

Analytical methods were developed that permitted the quantification of a wide variety of components with vastly differing chemical characteristics in both oil and aqueous samples. Octanol/water distribution coefficients for various phenols, nitrogen bases, and two-ring aromatic compounds were determined that were in close agreement with published literature values. Octanol/water distribution coefficients measured for monoaromatic hydrocarbons in this study were tabulated, but because they are hydrophobic, volatile, and present in aqueous phases only at low concentrations, the analytical method for aromatic hydrocarbon analysis was valid only for the less volatile, two-ring aromatic compounds. Because of their extreme water insolubility, saturated hydrocarbon K_{ow} data were not determined, although K_{bw} data were calculated for normal aliphatic hydrocarbons in three of the four oils studied.

Differences in component K_{bw} were observed among the four oils and can be attributed to differences in chemical composition among the oils. Components with polarities similar to that of the bulk oil remain highly associated with the parent oil upon equilibration with water, while components with polarities quite different from the bulk oil are not retained as strongly by the oil phase. For example, both the coal- and shale-derived fuels have much higher concentrations of polar, oxygen- and nitrogen-containing compounds than do the petroleum oils. These synthetic fuels also have higher K_{bw} for phenols and nitrogen bases.

A comparison of log K_{bw} of 1.22 for SRC II octanoic acid and 2.98 for SRC II C_3-substituted phenols, components with molecular weights similar to octanoic acid, shows that the more hydrophilic acids have lower K_{bw} than alkyl-substituted phenols of comparable molecular weight. Nitrogen bases have higher K_{bw} than phenols or acids of similar molecular weights, while aromatic hydrocarbons have still higher distribution coefficients. Saturated hydrocarbons have the highest K_{bw} of any of the compound classes examined in this study, but molecular clusters or aggregates complicate the oil/water determination of these components. The trend from low K_{bw} for acids to high coefficients for saturated hydrocarbons is the result of decreasing polarity and increasing lipophilicity.

For each component type, increasing alkyl substitution gives higher K_{bw}. Addition of each methyl group increases the molecular weight and the hydrophobic character of the molecule by a constant amount for a given compound type, thus giving log K_{bw} that increase linearily with increasing alkyl substitution. Saturated hydrocarbon log K_{bw} are all about 5, indicating that they partition into water from the oil very slightly. No linear trends for log K_{bw} are apparent with increasing molecular weight for saturated hydrocarbons. Aromatic hydrocarbons do show increasing log K_{bw} with increasing alkyl substitution but regression analysis does not show a very high correlation coefficient, due both to analytical difficulties caused by low aqueous phase concentrations and by the limited number of methyl groups that are found substituted on benzene or naphthalene.

Octanol/water distribution coefficients determined for each component in this study were quite consistent across all oils. For example, log K_{ow} determined for naphthalene were 3.50, 3.80, 3.73, and 3.39 for aqueous extracts of SRC II, Oxy, PBC, and No. 2 fuel oil, respectively. Calculation of the mean log K_{ow} and its associated standard deviation for naphthalene from each oil WSF in this study is 3.66 ± 0.19 while the mean of literature values is 3.28 ± 0.23.

Like log K_{bw}, log K_{ow} also increase linearily with increasing alkyl substitution within a compound class. Regression equations describing this trend can be used to estimate K_{ow} for alkyl-substituted components from the K_{ow} of the corresponding unsubstituted component. This trend is attributed to increasing lipophilicity as the molecular weight and nonpolar character of the molecule increases. Aliphatic carboxylic acid K_{ow} data determined in this study show a trend from low K_{ow} for low molecular weight acids to higher K_{ow} for heavier acids. However, the experimental log K_{ow} for hexanoic acid determined from an oil WSF in this study is higher than that for heptanoic acid. Further experiments showed this deviation in linearity was attributed to the presence of components other than acids in the samples.

Components having similar weights but representing different compound classes have different K_{ow}. Benzoic acid, an aromatic acid with no alkyl substitution and a molecular weight of 122, has a considerably lower K_{ow} than does hexanoic acid, which has a similar molecular weight. Benzoic acid has a log K_{ow} of 1.01 as determined from an SRC II WSF, a value at least lower by an order of magnitude than either quinoline (molecular weight 129) or C_2 phenol (molecular weight 122), which have log K_{ow} of 2.24 and 2.40, respectively. Aniline and phenol from an SRC II WSF have similar molecular weights but aniline has a much lower log K_{ow} (0.96) than phenol (1.43). Benzothiophene, molecular weight 134, and naphthalene, molecular weight 128, have similar log K_{ow} values of 3.34 and 3.50, respectively. Both benzothiophene and naphthalene are aromatic and have similar polarities.

Leo, Hansch, and Elkins (21) devote a section of their review article to the calculation of log K_{ow} from substituent constants added to a constant log K_{ow} for the unsubstituted aromatic compound. They report a substituent constant of -0.67 for a hydroxyl substituent and -1.23 for an amine substituent. Using their average literature value of 2.14 for log K_{ow} for benzene, substituent constants of -0.71 and -1.18 for hydroxyl and amine substituent constants were calculated in this study using SRC II log K_{ow} data. This method of adding substituent constants to the log K_{ow} for unsubstituted components can be used to estimate log K_{ow} of components that have no literature K_{ow} values published.

Peake and Hodgson (49) report a linear correlation of log aqueous solubility for saturated hydrocarbons with increasing molecular weight. Linear correlations are noted in this study for most component types, for both log K_{bw} and log K_{ow} with increasing alkyl substitution (molecular weight). These linear trends show how empirical relationships between log K_{ow} and log aqueous solubility, used by researchers such as Chiou et al., Mackay, and Veith et al. (11-14), are valid and can be used to estimate log K_{ow}.

Table 40 contains the slope and intercept values of linear regression equations relating log K_{ow} and alkyl substitution or carbon chain length for each compound type examined in this study. Intercepts for each of the component classes containing aromatic rings range from 0.96 for aniline to 3.51 to dicyclic aromatic hydrocarbons, but slopes are very similar for each component type, ranging from 0.425 to 0.492. The average slope for these regression equations is 0.457 ± 0.024.

TABLE 40. Slopes and Intercepts of Linear Regression Treatment of Log_{10} K_{ow} and Degree of Alkyl Substitution or Carbon Chain Length

Compound Type	Oil	Intercept	Slope
Phenol	SRC II	1.71	0.327
Aniline	SRC II	0.96	0.448
Quinoline	SRC II	2.22	0.425
Monocyclic aromatics	SRC II	2.11	0.492
Dicyclic aromatics	SRC II	3.51	0.457
Carboxylic acids (C_7-C_{11})	Oxy	-3.93	0.554

Compounds with similar K_{ow} would be expected to be bioaccumulated in lipid tissues of organisms to nearly the same extent if no elimination mechanisms, such as metabolism, were available to the organisms. Because different compounds are metabolized differently by organisms, K_{ow} data is useful for calculating the highest possible concentration a compound could reach in a biological system. Compounds such as sulfur heterocyclics and aromatic hydrocarbons can be expected to bioaccumulate to much greater concentrations than low molecular weight acids, phenols, and nitrogen bases, all of which have smaller K_{ow}. Octanol/water distribution coefficients are also useful in predicting sediment adsorption of organic compounds. Carboxylic acids, phenols, and nitrogen bases would not be expected to adsorb onto sediment particles to very high concentrations relative to concentrations in the water column, whereas an aromatic compound in this study, with a high K_{ow}, would be found in large relative concentrations adsorbed on particles. This phenomenon may, in some cases, affect the amount of organic compound available for biouptake by removing it from the water column. Both bioaccumulation and sediment adsorption are considered in modeling the fate of organic chemicals in an aquatic ecosystem.

This study shows that single component K_{ow} data for most compound types is useful in estimating the environmental behavior of those compounds, regardless of the source of aqueous contamination. Further, K_{ow} data for alkyl-substituted compounds may be estimated by applying an empirical equation to the K_{ow} for the corresponding unsubstituted compound. On the other hand, K_{bw} is dependent upon the fuel equilibrated with water, so that K_{bw} data for one fuel cannot be used to estimate data for a different oil. However, linear correlations of log K_{bw} with alkyl-substitution within a compound type should exist for any fuel. Therefore, K_{bw} data for alkyl-substituted components could be estimated from the K_{bw} for the unsubstituted component in that same oil/water system.

In an environmental system, both temperature and salinity, in the case of a marine system, would affect K_{bw} and K_{ow}, but the trends observed in this laboratory study would still exist.

Further study dealing with this research topic could include the development of methods allowing the use of larger samples for analysis of components present at very low concentrations. The analytical method for nitrogen bases could be expanded to incorporate very weak bases as well as neutral nitrogen-containing components. Methods for the accurate aqueous phase analysis of volatile components, such as the monocyclic aromatic hydrocarbons, could be developed. A method for the analysis of low molecular weight carboxylic acids could be developed. More detailed component identification studies could be conducted using extensive mass spectral examination and gas chromatographic retention time studies with authentic analytical standards.

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APPENDIX

MEASURED CONCENTRATIONS OF COMPONENTS IN OIL, OCTANOL, AND AQUEOUS PHASES

TABLE 1A. SRC II Phenol Concentrations in Oil, Octanol and Aqueous Phases

			Oil/Water		Octanol/Water	
Component	RRT[1]	Whole Oil[2]	Oil Phase[2]	Water Phase[3]	Octanol Phase[2]	Water Phase[3]
Phenol	1.0000	350 ± 3	16 ± 0.4	380 ± 16	81 ± 4.1	300 ± 13
o-Cresol	1.1754	160 ± 11	30 ± 0.4	160 ± 4	70 ± 3.9	76 ± 2.7
m-Cresol	1.2319	410 ± 23	66 ± 0.9	400 ± 8	160 ± 7	200 ± 0.0
p-Cresol	1.2446	230 ± 13	38 ± 0.5	230 ± 4	94 ± 3.9	110 ± 1
C_2 Phenol	1.3387	11 ± 1.8	5.6 ± 0.17	6.8 ± 0.19	4.5 ± 0.47	1.8 ± 0.14
2,6-Dimethylphenol	1.3475	43 ± 3.3	21 ± 0.2	30 ± 0.3	19 ± 1.1	6.6 ± 0.17
2,4-Dimethylphenol	1.3990	68 ± 4.3	32 ± 0.0	50 ± 0.4	31 ± 1.4	12 ± 0.2
C_2 Phenol	1.4090	100 ± 5	47 ± 0.1	72 ± 0.5	45 ± 1.8	18 ± 0.2
m-Ethylphenol	1.4261	210 ± 10	92 ± 0.2	150 ± 1	95 ± 3.6	40 ± 0.5
2-Isopropylphenol + p-Ethylphenol + 3,5-Dimethylphenol	1.4510	140 ± 6	64 ± 0.1	120 ± 2	83 ± 1.1	34 ± 0.8
3,4-Dimethylphenol	1.5202	83 ± 3.4	42 ± 0.8	55 ± 0.2	34 ± 1.2	15 ± 0.2
2,4,6-Trimethylphenol	1.5573	20 ± 2.0	18 ± 1.4	7.6 ± 0.05	5.9 ± 0.34	0.83 ± 0.03
C_3 Phenol	1.5639	26 ± 1.3	21 ± 0.3	10 ± 0.0	7.8 ± 0.33	1.1 ± 0.02
C_3 Phenol	1.5816	38 ± 1.9	31 ± 0.7	15 ± 0.0	11 ± 0.5	1.6 ± 0.03
C_3 Phenol	1.6043	49 ± 2.2	40 ± 0.9	19 ± 0.1	15 ± 0.5	2.1 ± 0.04
2,3,6-Trimethylphenol	1.6137	140 ± 5	120 ± 3	48 ± 0.2	39 ± 1.2	4.6 ± 0.07
C_3 Phenol	1.6287	170 ± 6	120 ± 3	68 ± 0.4	53 ± 1.6	8.5 ± 0.11
C_3 Phenol	1.6685	27 ± 1.4	23 ± 1.1	12 ± 0.1	7.8 ± 2.23	1.5 ± 0.05
C_4 Phenol	1.6995	8.3 ± 0.08	6.7 ± 0.13	3.6 ± 0.65	3.2 ± 0.02	0.52 ± 0.01
C_4 Phenol	1.7239	22 ± 0.5	18 ± 0.6	2.3 ± 0.94	2.5 ± 0.01	0.12 ± 0.01
C_4 Phenol	1.7410	22 ± 0.9	21 ± 2.9	4.6 ± 0.03	3.9 ± 0.11	0.26 ± 0.01
C_4 Phenol	1.7582	10 ± 2.2	12 ± 0.4	2.1 ± 0.02	1.2 ± 0.05	0.11 ± 0.00
C_4 Phenol	1.7847	99 ± 5.5	56 ± 1.5	57 ± 0.6	40 ± 1.3	12 ± 0.4
C_4 Phenol	1.7886	16 ± 0.7	25 ± 7.1	4.8 ± 2.07	3.1 ± 0.07	0.27 ± 0.01
C_5 Phenol	1.8445	13 ± 0.2	12 ± 1.1	1.0 ± 0.28	2.6 ± 0.14	0.23 ± 0.02
C_5 Phenol	1.9186	74 ± 2.8	71 ± 4.1	14 ± 0.2	12 ± 0.2	1.1 ± 0.03
C_5 Phenol	1.9458	nd[4]	nd	nd	nd	nd
C_5 Phenol	2.0133	21 ± 0.4	26 ± 2.4	4.7 ± 0.07	3.8 ± 0.74	0.16 ± 0.01
Indanol	1.8340	130 ± 3	75 ± 3.7	66 ± 1.0	51 ± 1.0	14 ± 0.3
C_1 Indanol	1.9801	39 ± 1.1	36 ± 1.8	11 ± 0.2	9.1 ± 0.14	1.31 ± 0.07
Total Selected Phenols		2700 ± 120	1200 ± 20	2000 ± 40	990 ± 34	870 ± 15

[1] Relative retention times with respect to phenol.
[2] Concentrations reported as µg/mL x 10^{-2}.
[3] Concentrations reported as µg/mL.
[4] Not determined.

TABLE 2A. Oxy Phenol Concentrations in Oil, Octanol and Aqueous Phases

			Oil/Water		Octanol/Water	
Component	RRT[1]	Whole Oil[2]	Oil Phase[2]	Water Phase[3]	Octanol Phase[2]	Water Phase[3]
Phenol	1.0000	140 ± 2	12 ± 0.6	1100 ± 110	36 ± 6.1	1000 ± 60
o-Cresol	1.1754	140 ± 1	35 ± 2.0	920 ± 51	68 ± 7.5	520 ± 17
m-Cresol	1.2319	190 ± 0.91	52 ± 0.7	1510 ± 78	89 ± 7.5	870 ± 15
p-Cresol	1.2446	140 ± 1	30 ± 0.5	1080 ± 56	65 ± 5.2	610 ± 18
C_2 Phenol	1.3387	28 ± 0.7	11 ± 2.8	140 ± 12	16 ± 4.4	47 ± 3.7
2,6-Dimethylphenol	1.3475	57 ± 0.3	22 ± 1.8	180 ± 5	19 ± 1.1	48 ± 2.9
2,4-Dimethylphenol	1.3990	190 ± 4.0	79 ± 5.2	880 ± 25	79 ± 2.7	250 ± 5
C_2 Phenol	1.4090	240 ± 2.7	100 ± 3	1130 ± 20	98 ± 2.4	300 ± 4
m-Ethylphenol	1.4261	53 ± 0.1	22 ± 0.2	390 ± 99	25 ± 2.1	86 ± 8.9
2-Isopropylphenol + p-Ethylphenol + 3,5-Dimethylphenol	1.4510	340 ± 1	140 ± 2	2180 ± 74	170 ± 7	570 ± 5
3,4-Dimethylphenol	1.5202	170 ± 3	64 ± 0.5	1060 ± 28	79 ± 2.3	360 ± 29
2,4,6-Trimethylphenol	1.5573	88 ± 0.1	79 ± 5.5	280 ± 11	28 ± 3.9	42 ± 9.1
C_3 Phenol	1.5639	85 ± 1.1	62 ± 1.7	210 ± 15	17 ± 0.2	29 ± 9.3
C_3 Phenol	1.5816	92 ± 1.5	60 ± 2.8	270 ± 27	22 ± 0.8	42 ± 20.0
C_3 Phenol	1.6043	160 ± 1	130 ± 4	520 ± 18	43 ± 0.9	79 ± 4.7
2,3,6-Trimethylphenol	1.6137	150 ± 1	87 ± 16.6	560 ± 20	58 ± 10.8	89 ± 9.9
C_3 Phenol	1.6287	140 ± 3	100 ± 3	500 ± 6	43 ± 0.4	66 ± 1.7
C_3 Phenol	1.6685	1020 ± 29	710 ± 21	3170 ± 71	290 ± 7	440 ± 14
C_4 Phenol	1.6995	61 ± 1.2	31 ± 1.3	390 ± 610	4.1 ± 0.88	nd[4]
C_4 Phenol	1.7239	20 ± 1.2	20 ± 0.6	170 ± 19	9 ± 1.7	47 ± 13.1
C_4 Phenol	1.7410	210 ± 8	130 ± 2	200 ± 72	64 ± 1.1	120 ± 28
C_4 Phenol	1.7582	15 ± 0.5	31 ± 1.6	760 ± 21	nd	nd
C_4 Phenol	1.7847	110 ± 3	85 ± 1.0	37 ± 10.4	5.5 ± 0.61	30 ± 14.9
C_4 Phenol	1.7886	12 ± 1.7	6.7 ± 0.38	480 ± 31	34 ± 0.7	120 ± 21
C_5 Phenol	1.8445	27 ± 1.0	24 ± 3.4	460 ± 328	71 ± 4.0	nd
C_5 Phenol	1.9186	28 ± 2.6	23 ± 4.8	220 ± 12	16 ± 0.4	50 ± 13
C_5 Phenol	1.9458	53 ± 1.6	43 ± 8.4	110 ± 54	6 ± 0.6	15 ± 6
C_5 Phenol	2.0133	30 ± 0.9	18 ± 4.3	130 ± 32	13 ± 0.9	12 ± 7.4
Indanol	1.8340	80 ± 2.6	170 ± 1	390 ± 32	29 ± 1.1	42 ± 7.7
C_1 Indanol	1.9801	170 ± 6	15 ± 2.5	190 ± 17	13 ± 0.3	60 ± 10
Total Selected Phenol		4000 ± 50	2400 ± 50	19600 ± 340	1510 ± 60	5900 ± 130

[1] Relative retention times with respect to phenol.
[2] Concentrations reported in µg/mL.
[3] Concentrations reported in ng/mL.
[4] Not determined.

TABLE 3A. PBC Phenol Concentrations in Oil, Octanol and Aqueous Phases

Component	RRT[1]	Whole Oil[2]	Oil/Water		Octanol/Water	
			Oil Phase[2]	Water Phase[3]	Octanol Phase[2]	Water Phase[3]
Phenol	1.0000	2.5 ± 0.12	0.7 ± 0.33	24 ± 1.3	0.9 ± 0.30	23 ± 4.9
o-Cresol	1.1754	6.2 ± 0.09	0.6 ± 0.09	57 ± 1.3	3.9 ± 0.18	31 ± 2.9
m-Cresol	1.2319	2.1 ± 0.15	1.0 ± 0.39	21 ± 0.8	1.5 ± 0.26	13 ± 2.0
p-Cresol	1.2446	2.7 ± 0.08	0.5 ± 0.18	25 ± 0.9	1.6 ± 0.18	14 ± 1.3
C_2 Phenol	1.3387	4.3 ± 0.36	1.2 ± 0.30	37 ± 0.8	2.7 ± 0.06	8.4 ± 0.75
2,6-Dimethylphenol	1.3475	2.5 ± 0.11	0.5 ± 0.25	17 ± 0.2	1.9 ± 0.23	4.5 ± 0.96
2,4-Dimethylphenol	1.3990	5.6 ± 0.15	1.4 ± 0.44	47 ± 1.2	4.4 ± 0.35	16 ± 2.0
C_2 Phenol	1.4090	10.1 ± 0.07	1.9 ± 0.21	100 ± 2	8.2 ± 0.41	24 ± 0.9
m-Ethylphenol	1.4261	0.8 ± 0.05	nd[4]	8.2 ± 0.06	0.7 ± 0.19	2.4 ± 0.78
2-Isopropylphenol + p-Ethylphenol + 3,5-Dimethylphenol	1.4510	1.8 ± 0.07	0.3 ± 0.15	18 ± 0.5	1.5 ± 0.11	3.9 ± 0.14
3,4-Dimethylphenol	1.5202	1.8 ± 0.06	1.0 ± 0.81	19 ± 0.2	1.4 ± 0.14	3.3 ± 0.12
2,4,6-Trimethylphenol	1.5573	9 ± 1.0	3.6 ± 0.25	59 ± 1.8	5.1 ± 0.33	5.5 ± 0.15
C_3 Phenol	1.5639	2.8 ± 0.04	0.9 ± 0.09	18 ± 0.5	1.9 ± 0.15	1.9 ± 0.10
C_3 Phenol	1.5816	3.4 ± 0.10	1.6 ± 0.42	24 ± 0.6	2.3 ± 0.21	2.0 ± 1.53
C_3 Phenol	1.6043	3.9 ± 0.13	1.6 ± 0.09	31 ± 1.4	2.7 ± 0.33	2.3 ± 0.15
2,3,6-Trimethylphenol	1.6137	2.7 ± 0.24	1.0 ± 0.37	18 ± 0.4	1.4 ± 0.22	1.6 ± 0.07
C_3 Phenol	1.6287	1.8 ± 0.24	1.0 ± 0.47	15 ± 2.0	1.5 ± 0.11	1.7 ± 0.25
C_3 Phenol	1.6685	8.1 ± 0.11	2.0 ± 0.28	61 ± 1.9	5.0 ± 0.41	5.6 ± 0.02
C_4 Phenol	1.6995	1.2 ± 0.06	0.7 ± 0.10	5.8 ± 0.17	0.3 ± 0.09	nd
C_4 Phenol	1.7239	3.9 ± 0.12	2.7 ± 0.86	16 ± 0.7	2.1 ± 0.54	nd
C_4 Phenol	1.7410	2.6 ± 0.18	1.6 ± 0.21	8 ± 3.8	0.6 ± 0.06	nd
C_4 Phenol	1.7582	1.8 ± 0.07	1.0 ± 0.05	7 ± 1.1	0.5 ± 0.11	nd
C_4 Phenol	1.7847	2.0 ± 0.47	1.1 ± 0.09	11 ± 1.0	0.8 ± 0.19	1.7 ± 0.00
C_4 Phenol	1.7886	2.0 ± 0.17	2.0 ± 0.89	20 ± 1.7	0.6 ± 0.23	2.9 ± 0.00
C_5 Phenol	1.8445	nd	nd	nd	nd	nd
C_5 Phenol	1.9186	0.7 ± 0.08	1.4 ± 0.58	6.9 ± 1.00	nd	nd
C_5 Phenol	1.9458	2.1 ± 0.12	1.7 ± 0.51	8.0 ± 0.35	1.3 ± 0.08	nd
C_5 Phenol	2.0133	nd	nd	1.3 ± 0.10	0.2 ± 0.11	1.2 ± 0.30
Indanol	1.8340	1.9 ± 0.13	0.7 ± 0.03	7.1 ± 0.08	0.6 ± 0.05	nd
C_1 Indanol	1.9801	1.2 ± 0.29	nd	nd	nd	nd
Total Selected Phenols		93 ± 1.2	40 ± 11	710 ± 14	56 ± 5.2	190 ± 21

[1] Relative retention times with respect to phenol.
[2] Concentrations reported in μg/mL.
[3] Concentrations reported in ng/mL.
[4] Not determined.

TABLE 4A. No. 2 Fuel Oil Phenol Concentrations in Oil, Octanol and Aqueous Phases

			Oil/Water		Octanol/Water	
Component	RRT[1]	Whole Oil[2]	Oil Phase[2]	Water Phase[3]	Octanol Phase[2]	Water Phase[3]
Phenol	1.0000	6.8 ± 0.20	nd	66 ± 4.9	2.5 ± 0.65	50 ± 2.4
o-Cresol	1.1754	23 ± 0.7	0.6 ± 0.09	230 ± 16	16 ± 0.8	110 ± 5
m-Cresol	1.2319	22 ± 0.2	0.5 ± 0.09	260 ± 16	20 ± 7.3	130 ± 5
p-Cresol	1.2446	9.3 ± 0.3	0.1 ± 0.07	110 ± 7	6.7 ± 0.2	55 ± 3.0
C_2 Phenol	1.3387	19 ± 0.6	3.4 ± 0.30	120 ± 6	11 ± 2.2	36 ± 3.7
2,6-Dimethylphenol	1.3475	12 ± 0.3	1.4 ± 0.08	110 ± 5	10 ± 2.2	25 ± 3.4
2,4-Dimethylphenol	1.3990	40 ± 0.6	4.4 ± 0.12	390 ± 13	35 ± 4.0	100 ± 3
C_2 Phenol	1.4090	44 ± 0.9	4.2 ± 0.11	470 ± 20	38 ± 1.6	120 ± 4
m-Ethylphenol	1.4261	13 ± 0.1	0.8 ± 0.04	160 ± 6	15 ± 3.6	42 ± 0.8
2-Isopropylphenol + p-Ethylphenol + 3,5-Dimethylphenol	1.4510	24 ± 0.1	1.6 ± 0.01	280 ± 4	26 ± 4.2	75 ± 0.9
3,4-Dimethylphenol	1.5202	24 ± 0.3	2.3 ± 0.26	280 ± 1	23 ± 1.1	77 ± 1.7
2,4,6-Trimethylphenol	1.5573	30 ± 1.5	10.6 ± 0.46	180 ± 2	15 ± 0.5	37 ± 3.1
C_3 Phenol	1.5639	12 ± 0.3	3.2 ± 0.43	100 ± 1	14 ± 9.1	11 ± 0.6
C_3 Phenol	1.5816	16 ± 0.4	3.8 ± 0.18	140 ± 1	23 ± 18	14 ± 0.3
C_3 Phenol	1.6043	22 ± 0.3	5.2 ± 0.48	200 ± 2	18 ± 1.2	21 ± 0.2
2,3,6-Trimethylphenol	1.6137	15 ± 0.9	5.2 ± 0.74	110 ± 2	10 ± 1.1	13 ± 1.4
C_3 Phenol	1.6287	13 ± 0.2	2.1 ± 0.14	140 ± 4	14 ± 2.5	16 ± 0.4
C_3 Phenol	1.6685	44 ± 0.9	11 ± 0.2	360 ± 7	32 ± 0.5	29 ± 13
C_4 Phenol	1.6995	2.3 ± 0.60	2.2 ± 0.29	13 ± 0.1	1.2 ± 0.75	2.2 ± 0.20
C_4 Phenol	1.7239	10 ± 0.0	4.0 ± 1.73	68 ± 3.3	5.6 ± 0.31	nd
C_4 Phenol	1.7410	nd[4]	nd	26 ± 1.8	nd	4.4 ± 0.61
C_4 Phenol	1.7582	3.4 ± 0.17	nd	29 ± 0.7	4.3 ± 0.81	nd
C_4 Phenol	1.7847	nd	nd	40 ± 0.7	3.5 ± 0.60	4.2 ± 0.39
C_4 Phenol	1.7886	nd	nd	63 ± 4.0	8.9 ± 6.62	5.8 ± 0.13
C_5 Phenol	1.8445	3.7 ± 0.71	3.0 ± 0.55	13 ± 1.0	0.4 ± 0.09	nd
C_5 Phenol	1.9186	nd	nd	22 ± 1.4	2.1 ± 0.39	nd
C_5 Phenol	1.9458	nd	nd	7 ± 1.2	nd	nd
C_5 Phenol	2.0133	nd	nd	24 ± 1.4	1.7 ± 0.07	nd
Indanol	1.8340	6.6 ± 0.28	3.9 ± 0.43	55 ± 5.9	4.1 ± 0.16	5.0 ± 1.13
C_1 Indanol	1.9801	4 ± 1.3	2.1 ± 0.15	26 ± 0.6	1.9 ± 0.03	nd
Total Selected Phenols		430 ± 7	95 ± 6.7	4100 ± 70	360 ± 69	990 ± 39

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[1] Relative retention times with respect to phenol.
[2] Concentrations reported in μg/mL.
[3] Concentrations reported in ng/mL.
[4] Not determined.

TABLE 5A. SRC II Nitrogen Base Concentrations in Oil, Octanol, and Aqueous Phases

Component	RRT[1]	Whole Oil[2]	Oil/Water Oil Phase[2]	Oil/Water Water Phase[2]	Octanol/Water Octanol Phase[2]	Octanol/Water Water Phase[2]
C_2 Pyridine	0.9132	nd	510 ± 77	1.8 ± 0.10	66 ± 10	1.3 ± 0.06
Aniline	1.0000	2200 ± 200	230 ± 30	13 ± 2.3	120 ± 16	13 ± 0.2
C_3 Pyridine	1.1062	140 ± 18	160 ± 21	0.45 ± 0.02	13 ± 1.8	0.3 ± 0.02
C_1 Aniline	1.4223	3800 ± 360	710 ± 78	21 ± 2.7	420 ± 49	17 ± 0.4
C_1 Aniline	1.4469	1800 ± 170	320 ± 33	9.1 ± 1.11	200 ± 21	7.3 ± 0.17
C_4 Pyridine	1.6218	90 ± 30	38 ± 4.1	0.08 ± 0.09	1.3 ± 0.11	0.1 ± 0.00
C_2 Aniline	1.8666	1400 ± 120	550 ± 56	5.1 ± 0.35	220 ± 23	2.8 ± 0.07
C_2 Aniline	1.8938	1600 ± 140	680 ± 70	5.6 ± 0.27	240 ± 26	3.1 ± 0.08
C_2 Aniline	1.9106	390 ± 38	150 ± 12	1.1 ± 0.06	46 ± 4.9	0.5 ± 0.01
C_2 Aniline	2.0155	260 ± 42	79 ± 6.2	0.6 ± 0.23	26 ± 2.6	0.5 ± 0.01
Quinoline	2.2034	1800 ± 180	1700 ± 160	2.0 ± 0.10	120 ± 12	0.7 ± 0.00
Isoquinoline + C_3 Aniline	2.3096	900 ± 100	710 ± 60	1.0 ± 0.05	65 ± 6.6	0.3 ± 0.03
C_1 Quinoline	2.5389	2100 ± 290	2100 ± 180	1.1 ± 0.08	84 ± 7.9	0.2 ± 0.00
C_1 Quinoline	2.7370	1100 ± 90	1400 ± 68	0.9 ± 0.10	60 ± 5.4	0.2 ± 0.00
C_1 Quinoline	2.7642	1500 ± 140	1070 ± 81	0.4 ± 0.03	33 ± 5.8	0.1 ± 0.00
C_1 Quinoline	2.9326	470 ± 29	550 ± 41	0.2 ± 0.02	15 ± 1.5	0.03 ± 0.00
C_2 Quinoline	3.0440	1200 ± 190	1400 ± 110	0.3 ± 0.04	25 ± 3.6	0.02 ± 0.00
C_3 Quinoline	3.6062	150 ± 12	170 ± 13	0.1 ± 0.01	7.4 ± 0.65	0.03 ± 0.00
Total Selected Nitrogen Bases		20000 ± 1300	13000 ± 1010	64 ± 9.6	1800 ± 190	47 ± 1.0

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[1] Relative retention times with respect to aniline.
[2] Concentrations reported in µg/mL.
[3] Not determined.

TABLE 6A. Oxy Nitrogen Base Concentrations in Oil, Octanol, and Aqueous Phases

Component	RRT[1]	Whole Oil[2]	Oil/Water		Octanol/Water	
			Oil Phase[2]	Water Phase[3]	Octanol Phase[2]	Water Phase[3]
C_2 Pyridine	0.9132	nd[4]	nd	nd	nd	nd
Aniline	1.0000	nd	nd	nd	nd	13 ± 2.7
C_3 Pyridine	1.1062	70 ± 2	nd	nd	11 ± 0.3	500 ± 66
C_1 Aniline	1.4223	nd	nd	nd	12 ± 0.4	250 ± 41
C_1 Aniline	1.4469	nd	nd	nd	1.5 ± 2.34	10 ± 4.1
C_4 Pyridine	1.6218	10 ± 1.5	nd	19 ± 2.1	2.3 ± 0.90	10 ± 1.9
C_2 Aniline	1.8666	nd	nd	36 ± 2.7	1.9 ± 0.12	20 ± 3.3
C_2 Aniline	1.8938	11 ± 1.0	5.3 ± 0.23	20 ± 1.6	nd	11 ± 0.8
C_2 Aniline	1.9106	49 ± 3.4	18 ± 1.0	89 ± 5.8	9 ± 1.1	54 ± 6.7
C_2 Aniline	2.0155	9 ± 1.4	4.3 ± 0.38	17 ± 2.8	1.6 ± 0.20	6.4 ± 0.66
Quinoline	2.2034	73 ± 2.5	16 ± 1.3	320 ± 21	15 ± 0.9	170 ± 26
Isoquinoline	2.3096	49 ± 1.3	8.3 ± 0.31	33 ± 2.2	2.7 ± 0.11	12 ± 1.2
C_1 Quinoline	2.5389	110 ± 6	38 ± 3.8	330 ± 27	29 ± 1.3	150 ± 15
C_1 Quinoline	2.7370	57 ± 3.8	49 ± 5.2	140 ± 13	14 ± 0.6	29 ± 2.3
C_1 Quinoline	2.7642	39 ± 5.1	20 ± 1.9	110 ± 13	9.3 ± 0.41	39 ± 3.9
C_1 Quinoline	2.9326	170 ± 13	100 ± 13	300 ± 35	26 ± 1.0	82 ± 6.3
C_2 Quinoline	3.0440	290 ± 21	180 ± 27	210 ± 32	34 ± 0.9	120 ± 8.4
C_3 Quinoline	3.6062	280 ± 65	210 ± 21	170 ± 24	11 ± 4.9	13 ± 8.7
Total Selected Nitrogen Bases		1200 ± 60	670 ± 88	2300 ± 380	180 ± 9	1500 ± 140

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[1] Relative retention times with respect to aniline.
[2] Concentrations reported in μg/mL.
[3] Concentrations reported in ng/mL.
[4] Not determined.

TABLE 7A. No. 2 Fuel Oil Nitrogen Base Concentrations in Oil, Octanol, and Aqueous Phases

Component	RRT[1]	Whole Oil[2]	Oil/Water		Octanol/Water	
			Oil Phase[3]	Water Phase[3]	Octanol Phase[3]	Water Phase[3]
C_2 Pyridine	0.9132	nd[4]	nd	nd	nd	nd
Aniline	1.0000	nd	140 ± 5	13 ± 0.5	180 ± 31	13 ± 2.3
C_3 Pyridine	1.1062	nd	nd	nd	nd	nd
C_1 Aniline	1.4223	nd	140 ± 17	59 ± 1.6	360 ± 71	45 ± 5.8
C_1 Aniline	1.4469	nd	nd	nd	nd	nd
C_4 Pyridine	1.6218	nd	nd	nd	nd	nd
C_2 Aniline	1.8666	11 ± 2.3	580 ± 65	58 ± 2.6	1100 ± 190	36 ± 4.6
C_2 Aniline	1.8938	11 ± 1.9	570 ± 60	56 ± 2.4	700 ± 140	34 ± 4.1
C_2 Aniline	1.9106	4 ± 1.2	400 ± 55	29 ± 1.3	220 ± 51	17 ± 1.9
C_2 Aniline	2.0155	3.8 ± 0.88	100 ± 25	18 ± 1.2	190 ± 52	8 ± 5.2
Quinoline	2.2034	9.2 ± 0.99	630 ± 32	38 ± 2.4	1300 ± 240	18 ± 2.1
Isoquinoline + C_3 Aniline	2.3096	5 ± 1.2	530 ± 55	22 ± 1.1	380 ± 170	6.1 ± 0.82
C_1 Quinoline	2.5389	6 ± 1.2	810 ± 210	22 ± 1.2	1100 ± 190	8.4 ± 0.90
C_1 Quinoline	2.7370	8 ± 1.5	1900 ± 320	20 ± 1.7	1100 ± 170	4.1 ± 0.91
C_1 Quinoline	2.7642	7 ± 1.0	1200 ± 180	18 ± 0.5	900 ± 140	5.3 ± 0.78
C_1 Quinoline	2.9326	6 ± 1.0	1500 ± 310	10 ± 0.9	370 ± 65	4.2 ± 2.20
C_2 Quinoline	3.0440	9 ± 1.5	2000 ± 370	9 ± 2.3	570 ± 85	2.9 ± 1.58
C_3 Quinoline	3.6062	nd	nd	nd	nd	nd
Total Selected Nitrogen Bases		90 ± 18	1100 ± 110	410 ± 16	860 ± 13	240 ± 25

[1] Relative retention times with respect to aniline.
[2] Concentrations reported in µg/mL.
[3] Concentrations reported in ng/mL.
[4] Not determined.

TABLE 8A. SRC II Saturated Hydrocarbon Concentrations in Oil and Aqueous Phases

Component	RRT[1]	Whole Oil[2]	Oil Phase[2]	Water Phase[3]
C_8	0.2588	95 ± 6	88 ± 4	0.7 ± 0.11
C_9	0.3528	370 ± 6	330 ± 7	3.5 ± 0.30
C_{10}	0.4641	1000 ± 48	930 ± 32	9.2 ± 0.64
C_{11}	0.5795	1760 ± 38	1920 ± 49	18 ± 1.3
C_{12}	0.6924	2300 ± 200	2200 ± 250	24 ± 2.0
C_{13}	0.8006	2410 ± 83	2600 ± 120	25 ± 3.1
C_{14}	0.9030	2600 ± 110	2840 ± 90	27 ± 2.8
C_{15}	1.0000	2200 ± 45	2400 ± 270	24 ± 2.5
C_{16}	1.0917	1760 ± 50	1580 ± 34	18 ± 2.0
C_{17}	1.1788	930 ± 19	880 ± 11	18 ± 1.4
Pristane	1.1789	290 ± 15	300 ± 11	3.1 ± 0.41
C_{18}	1.2616	550 ± 23	530 ± 18	6.1 ± 1.33
Phytane	1.2703	nd[4]	52 ± 0	nd
C_{19}	1.3402	390 ± 9	390 ± 9	3.9 ± 0.58
C_{20}	1.4152	350 ± 16	360 ± 4	3.4 ± 0.51
C_{21}	1.4869	240 ± 96	290 ± 8	2.8 ± 0.44
C_{22}	1.5552	200 ± 14	210 ± 10	1.2 ± 0.69
C_{23}	1.6207	nd	160 ± 13	nd
C_{24}	1.6840	nd	130 ± 11	nd
C_{25}	1.7493	nd	nd	nd
C_{26}	1.8193	nd	nd	nd
Total Selected Saturated Hydrocarbons		170×10^2	180×10^2	180 ± 18

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[1] Relative retention times with respect to C_{15}.

[2] Concentrations reported in µg/mL.

[3] Concentrations reported in ng/mL.

[4] Not determined.

TABLE 9A. Oxy Saturated Hydrocarbon Concentrations in Oil Phases

Component	RRT[1]	Whole Oil[2]	Oil Phase[2]
C_8	0.2588	nd[3]	nd
C_9	0.3528	35 ± 1	32 ± 3
C_{10}	0.4641	160 ± 8	160 ± 17
C_{11}	0.5795	540 ± 29	540 ± 37
C_{12}	0.6924	1420 ± 49	1440 ± 87
C_{13}	0.8006	2510 ± 38	2540 ± 65
C_{14}	0.9030	3520 ± 60	3540 ± 11
C_{15}	1.0000	4100 ± 130	4100 ± 110
C_{16}	1.0917	4400 ± 220	4200 ± 360
C_{17}	1.1788	5510 ± 300	5200 ± 570
Pristane	1.1789	6000 ± 330	5600 ± 620
C_{18}	1.2616	4800 ± 240	4500 ± 570
Phytane	1.2703	3900 ± 220	3600 ± 480
C_{19}	1.3402	5800 ± 270	5400 ± 700
C_{20}	1.4152	6500 ± 290	5900 ± 800
C_{21}	1.4869	6100 ± 230	5600 ± 730
C_{22}	1.5552	5500 ± 140	4900 ± 650
C_{23}	1.6207	5300 ± 250	4700 ± 500
C_{24}	1.6840	6000 ± 140	5500 ± 700
C_{25}	1.7493	8000 ± 1100	7000 ± 1800
C_{26}	1.8193	4000 ± 400	3400 ± 240
Total Selected Saturated Hydrocarbons		840 ± 33 x 10^2	770 ± 84 x 10^2

[1] Relative retention time with respect to C_{15}.
[2] Concentrations are reported as μg/mL.
[3] Not determined.

TABLE 10A. PBC Saturated Hydrocarbon Concentrations in Oil and Aqueous Phases

Component	RRT[1]	Whole Oil[2]	Oil Phase[2]	Water Phase[3]
C_8	0.2588	2700 ± 180	3000 ± 280	4.2 ± 0.44
C_9	0.3528	3550 ± 54	3900 ± 260	nd[4]
C_{10}	0.4641	3700 ± 110	4000 ± 110	nd
C_{11}	0.5795	3500 ± 110	3900 ± 130	3.2 ± 0.14
C_{12}	0.6924	3200 ± 51	3500 ± 63	3.3 ± 0.02
C_{13}	0.8006	3710 ± 51	3800 ± 200	2.6 ± 0.18
C_{14}	0.9030	3280 ± 10	3330 ± 27	2.7 ± 0.19
C_{15}	1.0000	2800 ± 380	2950 ± 14	1.9 ± 0.16
C_{16}	1.0917	2570 ± 42	2570 ± 74	1.8 ± 0.17
C_{17}	1.1788	3300 ± 210	2000 ± 330	1.6 ± 0.18
Pristane	1.1789	2100 ± 230	1300 ± 170	1.2 ± 0.16
C_{18}	1.2616	1600 ± 69	1610 ± 63	2.2 ± 0.52
Phytane	1.2703	810 ± 52	840 ± 31	0.7 ± 0.09
C_{19}	1.3402	1600 ± 160	1670 ± 87	1.7 ± 0.25
C_{20}	1.4152	1900 ± 270	2000 ± 120	1.7 ± 0.31
C_{21}	1.4869	1900 ± 310	1900 ± 290	1.9 ± 0.35
C_{22}	1.5552	2000 ± 290	1870 ± 76	2.2 ± 0.47
C_{23}	1.6207	2000 ± 360	1800 ± 110	2.1 ± 0.50
C_{24}	1.6840	3000 ± 430	2300 ± 530	1.9 ± 0.41
C_{25}	1.7493	2400 ± 1000	1800 ± 180	1.9 ± 0.41
C_{26}	1.8193	1490 ± 57	1300 ± 120	1.3 ± 0.14
Total Selected Saturated Hydrocarbons		550 ± 1 x 10^2	530 ± 31 x 10^2	40 ± 2.8

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[1] Relative retention times with respect to C_{15}.
[2] Concentrations reported in μg/mL.
[3] Concentrations reported in ng/mL.
[4] Not determined.

TABLE 11A. No. 2 Fuel Oil Saturated Hydrocarbon Concentrations in Oil and Aqueous Phases

Component	RRT[1]	Whole Oil[2]	Oil Phase[2]	Water Phase[3]
C_8	0.2588	490 ± 32	500 ± 6	nd[4]
C_9	0.3528	1800 ± 120	1800 ± 24	5 ± 1.7
C_{10}	0.4641	5300 ± 300	5220 ± 68	12 ± 9.4
C_{11}	0.5795	8900 ± 140	8630 ± 81	20 ± 12
C_{12}	0.6924	10400 ± 99	10000 ± 270	26 ± 4.6
C_{13}	0.8006	10900 ± 78	10900 ± 320	40 ± 11
C_{14}	0.9030	11900 ± 100	10900 ± 70	60 ± 29
C_{15}	1.0000	12900 ± 150	11100 ± 87	80 ± 44
C_{16}	1.0917	13900 ± 200	11200 ± 57	90 ± 53
C_{17}	1.1788	13700 ± 280	10800 ± 96	90 ± 54
Pristane	1.1789	4800 ± 120	4000 ± 32	30 ± 19
C_{18}	1.2616	11900 ± 240	1000 ± 220	80 ± 47
Phytane	1.2703	4180 ± 78	3480 ± 70	20 ± 16
C_{19}	1.3402	10600 ± 210	9700 ± 360	70 ± 43
C_{20}	1.4152	9000 ± 84	8900 ± 400	50 ± 30
C_{21}	1.4869	4650 ± 57	4800 ± 260	30 ± 17
C_{22}	1.5552	2650 ± 71	2800 ± 170	17 ± 9.4
C_{23}	1.6207	1400 ± 63	1600 ± 79	10 ± 2.5
C_{24}	1.6840	440 ± 29	750 ± 73	nd
C_{25}	1.7493	nd	230 ± 27	nd
C_{26}	1.8193	nd	nd	nd
Total Selected Saturated Hydrocarbons		140 ± 1×10^3	130 ± 1×10^3	700 ± 380

[1] Relative retention times with respect to C_{15}.
[2] Concentrations reported in μg/mL.
[3] Concentrations reported in ng/mL.
[4] Not determined.

TABLE 12A. SRC II Aromatic Hydrocarbon Concentrations in Oil, Octanol and Aqueous Phases

		Oil/Water			Octanol/Water	
Component	RRT[1]	Whole Oil[2]	Oil Phase[2]	Water Phase[3]	Octanol Phase[2]	Water Phase[3]
Ethylbenzene	0.4635	600 ± 130	590 ± 6	80 ± 14	22 ± 4.3	9 ± 3.33
m+p-Xylene	0.4739	1100 ± 230	1150 ± 11	140 ± 26	44 ± 7.9	12 ± 4.9
o-Xylene	0.5104	1200 ± 210	1150 ± 4	180 ± 35	50 ± 8.9	14 ± 6.1
Isopropylbenzene	0.5581	170 ± 14	200 ± 29	8.0 ± 1.5	20 ± 3.8	2.7 ± 0.36
1-Ethyl-4-methylbenzene	0.6203	1500 ± 140	1300 ± 470	80 ± 17	27 ± 3.5	9 ± 1.6
1,2,4-Trimethylbenzene	0.6716	2200 ± 190	2180 ± 22	140 ± 28	44 ± 4.7	7 ± 2.9
Secondary butylbenzene	0.7005	110 ± 10	96 ± 5	2.5 ± 0.2	1.4 ± 0.2	2.2 ± 0.32
1-Methyl-4-isopropylbenzene	0.7225	120 ± 10	120 ± 1	3.2 ± 0.8	1.0 ± 0.1	0.2 ± 0.15
1,3-Dimethyl-5-ethylbenzene	0.7787	1170 ± 82	1070 ± 11	20 ± 9.0	5.9 ± 1.0	1.0 ± 0.84
1,2-Diethylbenzene	0.7863	650 ± 47	590 ± 3	17 ± 3.3	4.1 ± 0.7	0.7 ± 0.23
1,2-Dimethyl-5-ethylbenzene	0.8256	4000 ± 290	3630 ± 19	160 ± 31	40 ± 5.4	6 ± 2.6
1,2,3,5-Tetramethylbenzene	0.8853	300 ± 200	370 ± 31	13 ± 2.2	3.3 ± 0.4	0.3 ± 0.12
Naphthalene	1.0000	18000 ± 1100	16300 ± 95	2000 ± 250	470 ± 38	150 ± 26
2-Methylnaphthalene	1.1748	29000 ± 1800	26100 ± 190	1200 ± 120	250 ± 27	26 ± 4.7
1-Methylnaphthalene	1.2029	5900 ± 360	5250 ± 30	240 ± 22	58 ± 5.4	6.2 ± 0.99
Biphenyl	1.2999	8900 ± 630	8090 ± 56	250 ± 17	58 ± 7.9	4.4 ± 0.82
1+2-Ethylnaphthalene	1.3175	28700 ± 970	25500 ± 99	730 ± 50	160 ± 25	14 ± 2.3
2,6-Dimethylnaphthalene	1.3388	9200 ± 700	8320 ± 48	160 ± 13	34 ± 8.2	1.0 ± 0.24
1,3-Dimethylnaphthalene	1.3629	4200 ± 350	3820 ± 33	73 ± 5.6	15 ± 3.8	1.3 ± 0.47
1,7-Dimethylnaphthalene	1.3682	3400 ± 240	3700 ± 920	56 ± 5.1	11 ± 3.0	0.4 ± 0.14
1,4-Dimethylnaphthalene	1.3778	4700 ± 400	4070 ± 25	74 ± 5.3	14 ± 4.0	0.3 ± 0.09
1,2-Dimethylnaphthalene	1.3919	3300 ± 330	2700 ± 290	38 ± 4.7	7 ± 2.7	0.1 ± 0.13
2,3,5-Trimethylnaphthalene	1.5626	3100 ± 400	2440 ± 61	35 ± 3.6	5 ± 2.0	nd[4]
Fluorene	1.5930	5400 ± 520	4560 ± 69	95 ± 4.3	21 ± 4.2	0.8 ± 0.17
Phenanthrene	1.8464	14000 ± 1300	11200 ± 740	120 ± 5	40 ± 12	nd
Anthracene	1.8581	2500 ± 270	1540 ± 80	10 ± 1.9	4 ± 2.9	nd
1-Methylphenanthrene	2.0136	2800 ± 540	1500 ± 360	8.4 ± 0.7	3 ± 2.6	nd
Fluoranthene	2.1652	4500 ± 540	3200 ± 110	22 ± 1.6	6 ± 3.7	nd
Pyrene	2.2249	6000 ± 1200	5290 ± 29	42 ± 7.7	9 ± 4.7	nd
Benzothiophene	1.0089	970 ± 64	900 ± 4	60 ± 6.5	12 ± 1.1	5.2 ± 0.64
Dibenzothiophene	1.8434	5900 ± 610	4600 ± 480	86 ± 4.5	12 ± 6.4	nd
Total Selected Aromatic Hydrocarbons		1700 ± 110 x 10^2	1520 ± 16 x 10^2	6200 ± 670	1500 ± 200	280 ± 57

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[1] Relative retention times with respect to naphthalene.
[2] Concentrations reported in µg/mL.
[3] Concentrations reported in ng/mL.
[4] Not determined.

TABLE 13A. Oxy Aromatic Hydrocarbon Concentrations in Oil, Octanol and Aqueous Phases

		Oil/Water			Octanol/Water	
Component	RRT[1]	Whole Oil[2]	Oil Phase[2]	Water Phase[3]	Octanol Phase[2]	Water Phase[3]
Ethylbenzene	0.4635	nd[4]	nd	nd	nd	nd
m+p-Xylene	0.4739	31 ± 0.9	28 ± 4.2	10 ± 0.8	2 ± 1.4	4 ± 2.3
o-Xylene	0.5104	15 ± 1.7	14 ± 0.5	8.6 ± 0.9	1.5 ± 0.49	3 ± 1.8
Isopropylbenzene	0.5581	nd	nd	nd	nd	nd
1-Ethyl-4-methylbenzene	0.6203	nd	nd	nd	nd	nd
1,2,4-Trimethylbenzene	0.6716	nd	nd	22 ± 2.6	1.2 ± 0.22	0.3 ± 0.27
Secondary butylbenzene	0.7005	nd	nd	nd	nd	nd
1-Methyl-4-isopropylbenzene	0.7225	130 ± 6	130 ± 7	76 ± 6.2	3.0 ± 0.81	nd
1,3-Dimethyl-5-ethylbenzene	0.7787	nd	nd	nd	nd	nd
1,2-Diethylbenzene	0.7863	nd	nd	nd	nd	nd
1,2-Dimethyl-5-ethylbenzene	0.8256	20 ± 11	13 ± 1.1	3.2 ± 0.3	0.19 ± 0.01	nd
1,2,3,5-Tetramethylbenzene	0.8853	60 ± 1.8	64 ± 4.1	15 ± 0.9	1.2 ± 0.22	nd
Naphthalene	1.0000	560 ± 33	560 ± 31	690 ± 27	27 ± 2.2	4 ± 1.3
2-Methylnaphthalene	1.1748	450 ± 13	450 ± 70	78 ± 9	6.7 ± 0.41	0.5 ± 0.09
1-Methylnaphthalene	1.2029	480 ± 96	520 ± 69	190 ± 10	7.4 ± 0.65	0.5 ± 0.17
Biphenyl	1.2999	510 ± 48	470 ± 16	120 ± 8	4.5 ± 0.24	0.5 ± 0.05
1+2-Ethylnaphthalene	1.3175	nd	nd	nd	nd	nd
2,6-Dimethylnaphthalene	1.3388	550 ± 50	580 ± 35	61 ± 4.0	2.3 ± 0.07	nd
1,3-Dimethylnaphthalene	1.3629	580 ± 18	580 ± 32	64 ± 3.5	2.4 ± 0.12	nd
1,7-Dimethylnaphthalene	1.3682	1420 ± 28	1500 ± 110	160 ± 10	6.0 ± 0.27	0.3 ± 0.07
1,4-Dimethylnaphthalene	1.3778	360 ± 12	320 ± 68	10 ± 1.6	0.56 ± 0.32	nd
1,2-Dimethylnaphthalene	1.3919	390 ± 11	400 ± 36	26 ± 1.7	0.99 ± 0.04	nd
2,3,5-Trimethylnaphthalene	1.5626	810 ± 50	810 ± 48	14 ± 0.3	0.39 ± 0.12	nd
Fluorene	1.5930	400 ± 23	370 ± 16	54 ± 4.7	1.8 ± 0.05	nd
Phenanthrene	1.8464	1470 ± 35	1540 ± 3	77 ± 7.1	2.9 ± 0.27	0.6 ± 0.37
Anthracene	1.8581	1100 ± 62	1100 ± 51	18 ± 1.4	0.61 ± 0.46	0.3 ± 0.07
1-Methylphenanthrene	2.0136	650 ± 60	620 ± 5	7.1 ± 1.4	0.19 ± 0.10	nd
Fluoranthene	2.1652	1300 ± 190	1470 ± 90	3.5 ± 0.4	nd	nd
Pyrene	2.2249	2700 ± 780	1800 ± 170	5.3 ± 0.9	nd	nd
Benzothiophene	1.0089	130 ± 9	130 ± 9	110 ± 2	3.5 ± 0.21	1.7 ± 0.26
Dibenzothiophene	1.8434	1700 ± 290	1800 ± 300	150 ± 48	3.0 ± 1.57	4 ± 1.4
Total Selected Aromatic Hydrocarbons		160 ± 8 $\times 10^2$	150 ± 3 $\times 10^2$	1900 ± 180	82 ± 4.7	26 ± 9.1

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[1] Relative retention times with respect to naphthalene.
[2] Concentrations reported in μg/mL.
[3] Concentrations reported in ng/mL.
[4] Not determined.

TABLE 14A. PBC Aromatic Hydrocarbon Concentrations in Oil, Octanol and Aqueous Phases

Component	RRT[1]	Oil/Water			Octanol/Water	
		Whole Oil[2]	Oil Phase[2]	Water Phase[3]	Octanol Phase[2]	Water Phase[3]
Ethylbenzene	0.4635	1000 ± 120	1060 ± 81	120 ± 6	33 ± 7.5	4.6 ± 0.75
m+p-Xylene	0.4739	3200 ± 350	3500 ± 230	440 ± 55	110 ± 23	11 ± 1.4
o-Xylene	0.5104	1200 ± 130	1350 ± 79	230 ± 41	53 ± 10	8 ± 1.4
Isopropylbenzene	0.5581	250 ± 22	270 ± 16	13 ± 0.9	nd	nd
1-Ethyl-4-methylbenzene	0.6203	390 ± 27	420 ± 23	16 ± 1.4	5 ± 1.0	4.0 ± 0.41
1,2,4-Trimethylbenzene	0.6716	1470 ± 78	1590 ± 87	90 ± 16	23 ± 3.7	1.5 ± 0.33
Secondary butylbenzene	0.7005	180 ± 8	90 ± 12	2.2 ± 0.7	0.9 ± 0.2	0.5 ± 0.46
1-Methyl-4-isopropylbenzene	0.7225	600 ± 320	870 ± 47	60 ± 10	15 ± 1.9	1.9 ± 0.54
1,3-Dimethyl-5-ethylbenzene	0.7787	250 ± 13	280 ± 19	4.2 ± 0.3	1.4 ± 0.2	nd
1,2-Diethylbenzene	0.7863	280 ± 11	310 ± 16	4.5 ± 0.5	1.6 ± 0.2	nd
1,2-Dimethyl-5-ethylbenzene	0.8256	290 ± 11	310 ± 21	5.1 ± 0.6	1.6 ± 0.2	nd
1,2,3,5-Tetramethylbenzene	0.8853	320 ± 11	350 ± 21	6 ± 1.1	2.9 ± 0.3	nd
Naphthalene	1.0000	990 ± 76	1010 ± 57	140 ± 21	46 ± 3.5	8 ± 1.3
2-Methylnaphthalene	1.1748	1210 ± 82	1400 ± 120	63 ± 8.6	19 ± 1.1	1.6 ± 0.37
1-Methylnaphthalene	1.2029	1100 ± 46	1170 ± 66	58 ± 7.4	18 ± 0.7	1.6 ± 0.23
Biphenyl	1.2999	600 ± 170	500 ± 110	9.2 ± 0.9	2.9 ± 0.2	nd
1+2-Ethylnaphthalene	1.3175	450 ± 77	480 ± 84	3.7 ± 0.5	1.2 ± 0.1	nd
2,6-Dimethylnaphthalene	1.3388	1100 ± 390	1200 ± 280	9.8 ± 1.1	3.1 ± 0.3	nd
1,3-Dimethylnaphthalene	1.3629	1100 ± 120	1200 ± 180	13 ± 3.8	4.7 ± 0.4	0.1 ± 0.11
1,7-Dimethylnaphthalene	1.3682	900 ± 140	1000 ± 190	10 ± 0.9	3.3 ± 0.3	nd
1,4-Dimethylnaphthalene	1.3778	600 ± 180	700 ± 190	5.7 ± 0.6	1.8 ± 0.2	nd
1,2-Dimethylnaphthalene	1.3919	400 ± 140	500 ± 150	3.3 ± 0.3	1.1 ± 0.1	nd
2,3,5-Trimethylnaphthalene	1.5626	490 ± 18	520 ± 35	1.5 ± 0.1	0.2 ± 0.0	nd
Fluorene	1.5930	96 ± 7	120 ± 58	12 ± 4.3	0.3 ± 0.0	nd
Phenanthrene	1.8464	240 ± 15	270 ± 59	3.5 ± 0.2	1.1 ± 0.1	0.4 ± 0.13
Anthracene	1.8581	66 ± 5	96 ± 36	0.2 ± 0.1	nd	nd
1-Methylphenanthrene	2.0136	190 ± 10	200 ± 1	0.9 ± 0.1	0.3 ± 0.0	nd
Fluoranthene	2.1652	nd[4]	nd	nd	nd	nd
Pyrene	2.2249	nd	nd	nd	nd	nd
Benzothiophene	1.0089	290 ± 16	310 ± 19	6 ± 2.3	2.3 ± 0.3	0.5 ± 0.47
Dibenzothiophene	1.8434	1250 ± 37	1300 ± 56	14 ± 1.5	1.8 ± 0.5	2.2 ± 0.27
Total Selected Aromatic Hydrocarbons		200 ± 6 x 10^2	220 ± 22 x 10^2	1300 ± 190	350 ± 53	46 ± 6.0

[1] Relative retention times with respect to naphthalene.

[2] Concentrations reported in µg/mL.

[3] Concentrations reported in ng/mL.

[4] Not determined.

TABLE 15A. No. 2 Fuel Oil Aromatic Hydrocarbon Concentrations in Oil, Octanol and Aqueous Phases

	Oil/Water				Octanol/Water	
Component	RRT[1]	Whole Oil[2]	Oil Phase[2]	Water Phase[3]	Octanol Phase[2]	Water Phase[3]
Ethylbenzene	0.4635	280 ± 0	160 ± 10	46 ± 7.1	13 ± 3.1	9 ± 3.1
m+p-Xylene	0.4739	1130 ± 6	1190 ± 5	250 ± 33	70 ± 17	34 ± 8.8
o-Xylene	0.5104	510 ± 9	520 ± 4	140 ± 14	38 ± 8.0	27 ± 2.0
Isopropylbenzene	0.5581	2120 ± 90	630 ± 32	23 ± 6.7	19 ± 1.5	90 ± 13
1-Ethyl-4-methylbenzene	0.6203	nd	nd	nd	nd	nd
1,2,4-Trimethylbenzene	0.6716	4000 ± 41	3400 ± 130	250 ± 28	90 ± 15	51 ± 4.5
Secondary butylbenzene	0.7005	nd	nd	nd	nd	nd
1-Methyl-4-isopropylbenzene	0.7225	nd	nd	nd	nd	nd
1,3-Dimethyl-5-ethylbenzene	0.7787	900 ± 4	920 ± 21	17 ± 2.0	6 ± 1.4	2.7 ± 0.83
1,2-Diethylbenzene	0.7863	1800 ± 130	1630 ± 15	39 ± 4.9	14 ± 2.8	nd
1,2-Dimethyl-5-ethylbenzene	0.8256	2800 ± 32	2770 ± 17	100 ± 14	34 ± 5.8	9 ± 2.3
1,2,3,5-Tetramethylbenzene	0.8853	2530 ± 29	2510 ± 22	73 ± 11.0	26 ± 4.0	5.1 ± 0.76
Naphthalene	1.0000	2730 ± 10	2710 ± 28	580 ± 76	180 ± 5	70 ± 13
2-Methylnaphthalene	1.1748	6700 ± 38	6800 ± 190	400 ± 63	110 ± 6	16 ± 2.8
1-Methylnaphthalene	1.2029	3940 ± 9	4000 ± 106	230 ± 34	71 ± 3.4	11 ± 1.3
Biphenyl	1.2999	300 ± 200	500 ± 12	13 ± 1.8	3.9 ± 0.1	0.17 ± 0.02
1+2-Ethylnaphthalene	1.3175	2180 ± 1	2190 ± 59	36 ± 7.5	9.5 ± 0.9	nd
2,6-Dimethylnaphthalene	1.3388	3940 ± 57	4500 ± 120	80 ± 21	19 ± 2.8	nd
1,3-Dimethylnaphthalene	1.3629	4430 ± 52	4400 ± 140	90 ± 18	23 ± 1.6	1.5 ± 0.38
1,7-Dimethylnaphthalene	1.3682	2980 ± 50	3400 ± 280	60 ± 12	17 ± 1.2	1.6 ± 0.16
1,4-Dimethylnaphthalene	1.3778	2170 ± 95	2200 ± 33	41 ± 7.8	11 ± 1.0	2.7 ± 0.05
1,2-Dimethylnaphthalene	1.3919	680 ± 1	690 ± 41	16 ± 3.3	4.2 ± 0.3	0.5 ± 0.10
2,3,5-Trimethylnaphthalene	1.5626	1700 ± 110	1900 ± 120	15 ± 6.2	nd	nd
Fluorene	1.5930	750 ± 11	900 ± 204	10 ± 3.5	2.1 ± 0.2	nd
Phenanthrene	1.8464	1500 ± 110	1600 ± 180	21 ± 5.0	4.0 ± 1.2	nd
Anthracene	1.8581	nd	nd	nd	nd	nd
1-Methylphenanthrene	2.0136	nd	nd	nd	nd	nd
Fluoranthene	2.1652	nd	nd	nd	nd	nd
Pyrene	2.2249	nd	nd	nd	nd	nd
Benzothiophene	1.0089	2730 ± 13	880 ± 8	100 ± 12	25 ± 0.8	18 ± 0.8
Dibenzothiophene	1.8434	250 ± 18	1400 ± 161	24 ± 4.8	nd	nd
Total Selected Aromatic Hydrocarbons		530×10^{2}	520×10^{2}	2640	790	350

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[1] Relative retention times with respect to naphthalene.
[2] Concentrations reported in µg/mL.
[3] Concentrations reported in ng/mL.
[4] Not determined.

TABLE 16A. SRC II Acid Concentrations in Oil, Octanol and Aqueous Phases

		Oil/Water			Octanol/Water	
Component	RRT[1]	Whole Oil[2]	Oil Phase[2]	Water Phase[3]	Octanol Phase[2]	Water Phase[3]
Hexanoic acid	0.4611	12 ± 0.2	5.1 ± 0.66	600 ± 120	9.3 ± 0.47	610 ± 91
C_6 Acid	0.6215	0.9 ± 0.27	0.9 ± 0.11	54 ± 5	1.9 ± 0.48	8 ± 2
C_6 Acid	0.6953	1.9 ± 0.20	1.6 ± 0.17	110 ± 14	1.8 ± 0.21	15 ± 11
Heptanoic acid	0.7161	4.0 ± 0.08	1.2 ± 0.31	250 ± 23	1.7 ± 0.21	240 ± 21
C_7 Acid	0.7666	0.7 ± 0.02	0.3 ± 0.11	49 ± 4	0.2 ± 0.03	48 ± 5
C_7 Acid	0.7955	9.4 ± 1.2	5.6 ± 0.71	70 ± 5	18 ± 0.6	41 ± 3
Benzoic acid	0.9131	4.4 ± 1.19	1.3 ± 0.40	250 ± 45	2.3 ± 0.32	220 ± 26
Octanoic acid	1.0000	2.5 ± 0.08	1.6 ± 0.33	97 ± 7	1.9 ± 0.51	110 ± 10
C_8 Acid	1.1195	36 ± 2.2	31 ± 8.5	210 ± 15	57 ± 4.7	87 ± 10
C_1 Benzoic acid	1.1957	30 ± 3.3	22 ± 6.2	280 ± 31	43 ± 3.6	140 ± 34
Nonanoic acid	1.2903	2.0 ± 0.32	0.6 ± 0.10	27 ± 5	2.7 ± 0.42	31 ± 1
C_9 Acid	1.3023	6.6 ± 0.64	3 ± 1.3	39 ± 6	5.9 ± 0.92	10 ± 2
C_9 Acid	1.4090	1.1 ± 0.03	0.4 ± 0.16	26 ± 10	0.9 ± 0.04	19 ± 1
C_9 Acid	1.4451	2.6 ± 0.16	2.0 ± 0.06	27 ± 10	2.2 ± 0.31	nd
C_2 Benzoic acid	1.4924	1.1 ± 0.16	1.1 ± 0.08	80 ± 37	nd[4]	nd
Decanoic acid	1.5750	1.5 ± 0.05	1.6 ± 0.21	35 ± 10	1.9 ± 0.79	nd
Total Selected Acids		129 ± 6	80 ± 17.0	2200 ± 34	150 ± 4	1630 ± 25

[1] Relative retention times with respect to octanoic acid - methyl ester.
[2] Concentrations reported in μg/mL.
[3] Concentrations reported in ng/mL.
[4] Not determined.

TABLE 17A. Oxy Acid Concentrations in Oil, Octanol and Aqueous Phases

Component	RRT[1]	Oil/Water			Octanol/Water	
		Whole Oil[2]	Oil Phase[2]	Water Phase[2]	Octanol Phase[2]	Water Phase[2]
Hexanoic acid	0.4611	27 ± 2.3	27 ± 1.9	0.6 ± 0.14	66 ± 7	0.7 ± 0.12
Heptanoic acid	0.7161	24 ± 5.6	2.7 ± 0.39	2.5 ± 0.37	11 ± 1	2.8 ± 0.34
Octanoic acid	1.0000	80 ± 20	20 ± 0.8	7.5 ± 0.76	110 ± 4	8.7 ± 0.48
Nonanoic acid	1.2903	140 ± 32	82 ± 8.2	8.1 ± 0.83	490 ± 13	7 ± 1.2
Decanoic acid	1.5750	220 ± 27	210 ± 13	4.3 ± 0.39	960 ± 38	2.6 ± 0.64
Undecanoic acid	1.8476	64 ± 7.6	74 ± 8.5	0.5 ± 0.05	160 ± 24	0.2 ± 0.03
Total Selected Acids		560 ± 80	420 ± 28	24 ± 2.3	1800 ± 77	22 ± 2.6

[1] Relative retention times with respect to octanoic acid - methyl ester.

[2] Concentrations reported in µg/mL.

TABLE 18A. No. 2 Fuel Oil Acid Concentrations in Oil, Octanol and Water Phases

		Oil/Water			Octanol/Water	
Component	RRT[1]	Whole Oil[2]	Oil Phase[2]	Water Phase[2]	Octanol Phase[2]	Water Phase[2]
Heptanoic acid	0.6953	400 ± 100	180 ± 4	27 ± 1.4	660 ± 9	20
Benzoic acid	0.9131	1290 ± 96	1200 ± 170	65 ± 7.0	2930 ± 54	48
Octanoic acid	1.0000	600 ± 130	410 ± 18	30 ± 2.5	2300 ± 172	30
Nonanoic acid	1.2903	800 ± 130	800 ± 78	35 ± 0.3	3200 ± 320	23
C_9 Acid	1.3001	60 ± 11	140 ± 36	10 ± 0.1	400 ± 94	5.8
Decanoic acid	1.5750	700 ± 160	1000 ± 230	36 ± 5.8	4300 ± 280	20
Total Selected Acids		3800 ± 430	3600 ± 170	170 ± 47	13300 ± 150	150

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[1] Relative retention times with respect to octanoic acid - methyl ester.
[2] Concentrations reported in ng/mL.

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