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THE DISSOLUTION AND PHOTODEGRADATION OF KUWAIT CRUDE OIL IN SEAWATER

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**THE DISSOLUTION AND PHOTODEGRADATION OF
KUWAIT CRUDE OIL IN SEAWATER**

by

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B.Sc., M.Sc.

A thesis submitted to the University of Plymouth
in partial fulfilment for the degree of

DOCTOR OF PHILOSOPHY

Department of Environmental Sciences
Faculty of Science

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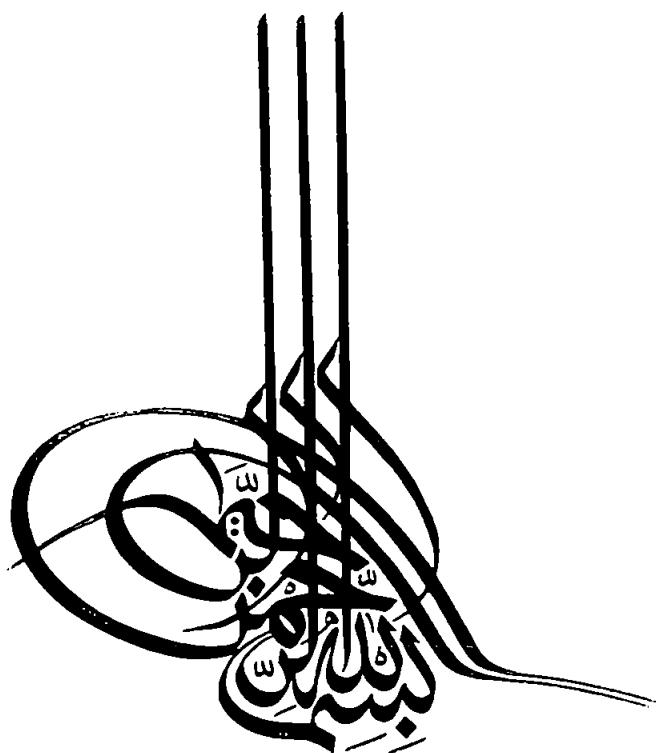
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***In the name of God,
Most Gracious, Most Merciful***

Praise be to Allah, the Lord of all the Worlds

I thank God for granting me the guidance, patience and determination to achieve this ambition, especially during the invasion and occupation of my beloved country Kuwait, and the difficult time being separated from my family.

*To My Parents,
Brothers and Sisters*

THE DISSOLUTION AND PHOTODEGRADATION OF KUWAIT CRUDE OIL IN SEAWATER

Lulwa Nasser Ali

ABSTRACT

To further a quantitative understanding of the effects of weathering on oil spilled at sea, a series of laboratory experiments were conducted to investigate the dissolution and photodegradation kinetics of Kuwait crude oil in seawater. A simple and practical method was developed for the preparation of stable homogeneous samples of seawater-soluble oil (SWSF) at 25 °C. The dissolution was monitored by two independent but complementary methods; total dissolved oil was measured by a photochemical dissolved organic carbon (DOC) technique whilst the dominant soluble constituents, aromatic hydrocarbons, were measured by ultraviolet-fluorescence (UVF) spectrophotometry. Maximum dissolution was observed after slowly stirring oil on seawater for 5 days when concentrations were, respectively, 3.2-3.6 $\mu\text{g C mL}^{-1}$ seawater (DOC) and 2.4 $\mu\text{g diesel equivalents mL}^{-1}$ seawater (UVF).

Quantification of the photodegradation of individual SWSF constituents required development and optimisation of a more specific analytical method. The final method involved addition of deuterated internal standards, extraction with *n*-pentane, controlled evaporation (micro Kuderna-Danish concentration) and gas chromatography-mass spectrometry (GC-MS). Particular care was taken to eliminate sample contamination and storage conditions were also optimised. The recovery of deuterated internal standards through the isolation steps ranged from 30% for benzene- d_6 to 100% for phenanthrene- d_{10} . The method allowed more than fifty compounds, mainly low molecular weight aromatic hydrocarbons, to be identified and quantified in the SWSF. Alkylated benzenes (C_{0-4}) were the most abundant (98% of the dissolved oil) followed by alkylated naphthalenes (C_{0-3}) ($\approx 2\%$). The oil to seawater partition coefficient of individual hydrocarbons (K_{ow}) showed that hydrocarbons of high aqueous solubility (e.g. C_{0-2} alkylbenzenes) also possessed the lowest partition values, whereas compounds with high partition coefficients (e.g. alkyl naphthalenes) remained mainly in the oil phase.

A reproducible method of simulating solar irradiation was established under controlled environmental conditions using a calibrated 1.8 kW xenon lamp. The photodegradation of a model SWSF compound (phenanthrene) followed first-order kinetics ($k_p = 0.317 \pm 0.029$) with a half life ($t_{1/2}$) of 2.2 hr at 25 °C when irradiated at 194 W m^{-2} . The extrapolation of $t_{1/2}$ to latitude 30 °N (Florida summer sunlight) showed that phenanthrene would degrade in ≈ 9 hr. Some photoproducts including fluorene, fluorenone, 2,2'-diformylbiphenyl, 2,3:4,5-dibenzoxepin, 3,4-benzocoumarin, and 9,10-phenanthrenequinone were identified by GC-MS, although these accounted for only 11% of the initial mass of phenanthrene. UVF and GC-MS methods for examining the photodegradation of phenanthrene were compared.

The photochemical fate of the characterised SWSF was investigated using the optimised irradiation system. Benzene and C_{0-3} alkylated benzenes showed no evidence of photodegradation after periods of up to 48 hour under the lamp, however, some C_4 alkylbenzenes (*sec*-butylbenzene, 1,2-dimethylbenzene, 1,2,4,5- + 1,2,3,4-tetramethylbenzene and 1,2,3,4-tetramethylbenzene) appeared to follow first-order kinetics with respect to irradiation time. The photodegradation rate constants (k_p) of the alkylated benzene and alkylated naphthalene isomers were statistically different demonstrating that certain isomers will photodegrade faster than others under the same conditions. Half lives ranged from 11.8 to 33.6 hr at 25 °C. The majority of naphthalene (i.e. C_{0-3}) identified in the SWSF of Kuwait crude oil exhibited first-order photodegradation kinetics with differing rate constants. Half lives were: naphthalene, 15.7 hr; 1-methyl and 2-methyl naphthalene, 14.9 and 12 hr, respectively; 1+2-ethylnaphthalene, 15.9; 1,6-dimethylnaphthalene, 10.4 hr; 1,3,7- and 1,2,4-trimethylnaphthalene, 11.95 and 12 hr, respectively. The low initial concentration of other naphthalene isomers did not allow for accurate photodegradation kinetics to be determined. Extrapolating the data to latitude 30 °N showed that the photodegradation $t_{1/2}$ expected for the determined SWSF compounds were between 4.2 to 7 days. This would make photodegradation an effective weathering process for the removal of spilled oil, particularly in high solar radiation environments.

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LIST OF ABBREVIATIONS AND SYMBOLS

Benzene-d ₆	Deuterated benzene
°C	Degrees Celcius
Cst	Centistokes
CTC	Charge transfer complex
ρ	Density
DCM	Dichloromethane
DOC	Dissolved organic carbon
EPA	Environmental Protection Agency
FID	Flame ionisation detector
GC-MS	Gas chromatography-mass spectrometry
HPLC	High performance liquid chromatography
hr	Hour
i.d.	Inner diameter
IR	Infrared
ITOPF	International Tankers Owners Pollution Federation
K-D	Kuderna-Danish
K_{ow}	Partition coefficient between octanol and water
$K_{oil/sw}$	Partition coefficient between oil and seawater
k_p	Photodegradation rate constant
LLE	Liquid-liquid extraction
m/z	Mass to charge ratio
MC	Mass chromatogram
μg	Microgram ($\times 10^{-6}$ g)
mg	Milligram ($\times 10^{-3}$ g)
mL	Millilitre ($\times 10^{-3}$ L)
m_{oil}	Mass of a hydrocarbon remaining in oil phase following equilibrium partitioning
m_{sw}	Mass of a hydrocarbon accumulating in water phase following equilibrium partitioning
m_t	Total mass of a hydrocarbon in oil phase before partitioning
n.d.	Not determined
Naphthalene-d ₈	Deuterated naphthalene
NAS	National Academy of Sciences
ng	Nanogram ($\times 10^{-9}$ g)
nm	Nanometre ($\times 10^{-9}$ m)
o.d.	Outer diameter
OWD	Oil-in-water dispersion
$^1\text{O}_2$	Singlet state oxygen
Phenanthrene-d ₁₀	Deuterated phenanthrene
ppm	Part per million (mg L^{-1} or $\mu\text{g mL}^{-1}$)
RI	Retention index
rpm	Revolution per minute
RRF	Relative response factor
RSD	Relative standard deviation
SD	Standard deviation
SE	Standard error of estimates
SWSF	Seawater soluble fraction
TIC	Total ion chromatogram
UVF	Ultraviolet fluorescence spectrophotometry
V_{oil}	Volume of oil
V_{sw}	Volume of seawater
WSF	Water soluble fraction

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diesel oils as UVF calibrants.

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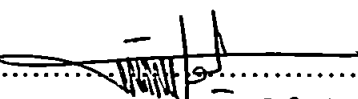
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Last but not least, I am very grateful to my parents who have shown a great deal of patience and understanding over my long period of study.

DECLARATION

I, Lulwa Nasser Ali, hereby declare that the following thesis is based on the results of experiments performed by myself and that the thesis is of my own composition, except where otherwise acknowledged and has not been previously presented, in part or in whole, for a higher degree. This study was financed by the Kuwait Institute for Scientific Research, Kuwait. The research was conducted in the Department of Environmental Sciences, University of Plymouth in collaboration with Plymouth Marine Laboratory under the supervision of Professor S.J. Rowland and Professor R.F.C. Mantoura.

Signed..........
Date.....18-5-1994.....

PREFACE

This thesis consists of six chapters. A general introduction, including the general aim of the study is given in Chapter one. A specific introduction, literature review and aims which deal specifically with the topic is given in the first section of each of the following chapters. This is followed by the experimental section, results and discussion and finally the conclusions in view of the results achieved for that chapter. Chapter six summarises the overall outcome of the study and focuses on areas for further study. References cited in the thesis are to be found after Chapter six. Some of the aspects of the work described in this thesis have been published or are in press (Ali *et al.*, 1993; Ali *et al.*, 1994).

A summary description of each chapter is given here.

Chapter 1

Introduces a brief overview of the research problem and highlights the importance of fate of oil studies and in particular photodegradation. The aims of the present study are given.

Chapter 2

Reviews the methods used previously for the preparation and monitoring of SWSF of oil and describes the factors that influence both concentration and composition of such solutions. Progressive developments undertaken to devise and optimise an experimental procedure for the dissolution of a Kuwait crude oil under carefully controlled conditions are described, and the monitoring of the dissolution by two independent but complementary methods; ultraviolet-fluorescence (UVF) spectroscopy and dissolved organic carbon (DOC) is discussed. The results of the two methods are compared and a conclusion drawn in view of the results.

Chapter 3

Describes the progressive assessments made for optimising and verifying an analytical methodology for the preparation and analysis of SWSF samples. A detailed characterisation of individual components in the SWSF by gas chromatography-mass spectrometry (GC-MS) is shown. The concentration of SWSF components is compared with their concentrations in the oil and the partition coefficients between the oil phase and seawater phase ($K_{oil/sw}$) determined and discussed.

Chapter 4

Details the development work undertaken to establish and validate a reproducible irradiation methodology using realistic and well controlled environmental irradiation conditions. The photodegradation rate constant (k_p) of a model SWSF compound (phenanthrene) is determined and the transformation photoproducts characterised and measured. A direct comparison between GC-MS and UVF methods for maintaining the photodegradation of phenanthrene is made.

Chapter 5

Focuses on the application of the established photolysis methodology to the determination of the rates of photodegradation and the half-lives of compounds of the characterised SWSF. The results provide the first detailed information on the photodegradation kinetics of a mixture of oil hydrocarbons in seawater made under the best available alternative to natural sunlight. An extrapolation of the kinetic data to different latitudes is described.

Chapter 6

Summarises the outcome of the study and highlights area for further study.

CHAPTER ONE

CHAPTER ONE

INTRODUCTION

1.1 General

During recent years, including the period of this research, there have been a number of major oil spills in various regions of the world (Figure 1.1). Analysis of the reasons for some of larger spills shows that about 75% were caused by groundings, collisions and contacts and about 8% by oil transfer operations (Figure 1.2). Oil spills in Shetland (1993, 85000 metric tonnes (t)), off Spain (1992, 70000 t), and in the Arabian Gulf (1990, 816000 t), are a poignant reminder of the threat posed to the marine environment from the resulting pollution (Pearce, 1993; SOAFD, 1993; Wolff *et al.*, 1993). Regardless of the enormous investment in research and development, oil pollution remains a continuing and unpredictable problem. Unfortunately, the main impact is often on ecologically fragile coastal areas where sites of specific ecological importance provide support for vulnerable industries, such as the marine culture facilities in Shetland (Fishing News, 1993), and power stations and desalination plants as exemplified during the Gulf War oil spill (Literathy, 1992).

The amount of oil in a spill provides one means of generally quantifying the potential for ecological damage. More specific factors include the following: oil composition; local salinity and depth of water; local average sea temperatures; time of year; wave energy; prevailing wind and current directions; relative purity of the environment; types of marine habitats that will come into contact with the oil; and most importantly, the speed and

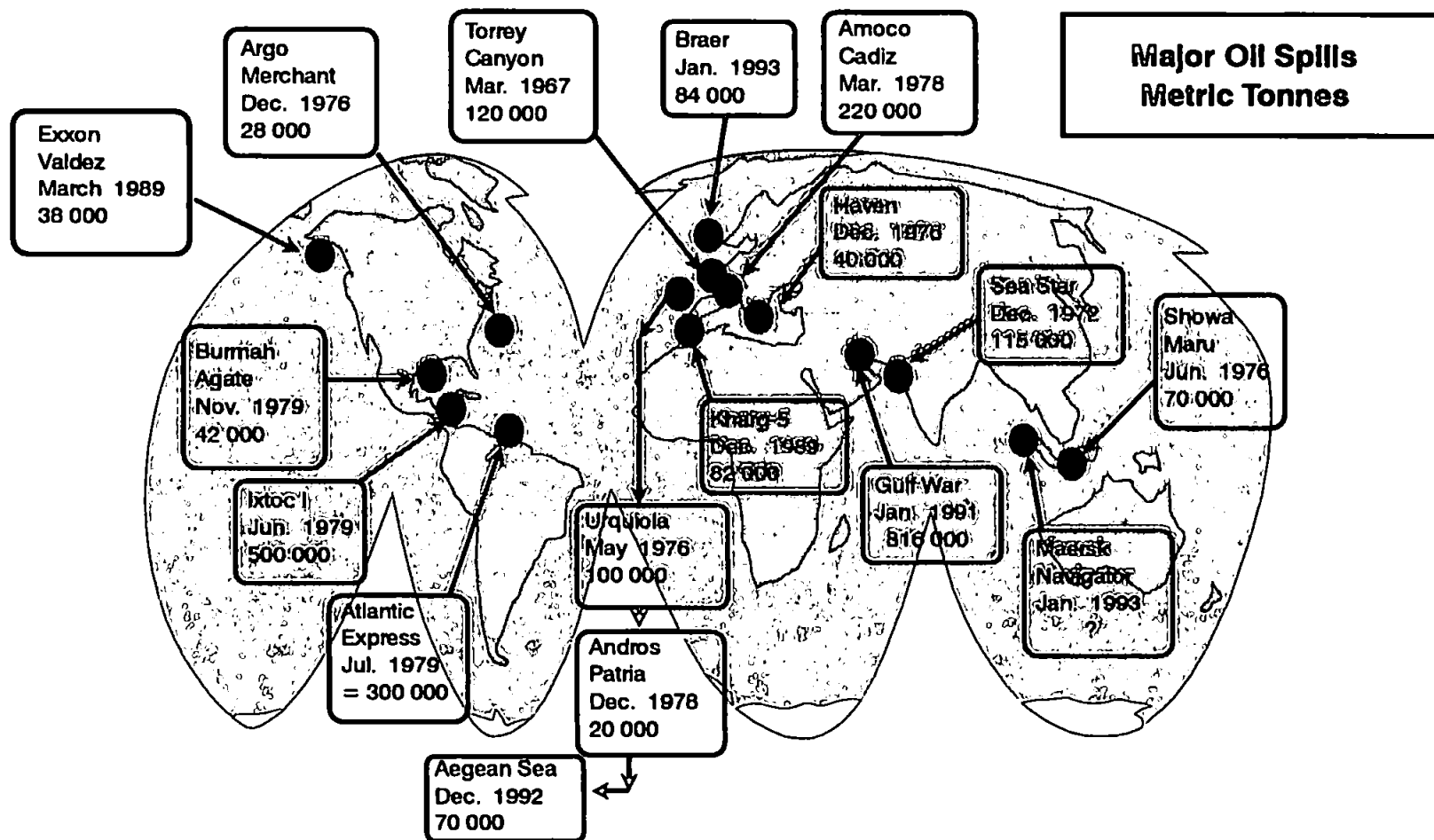


Figure 1.1 Major oil spills which have occurred in various regions of the world (Pearce, 1993).

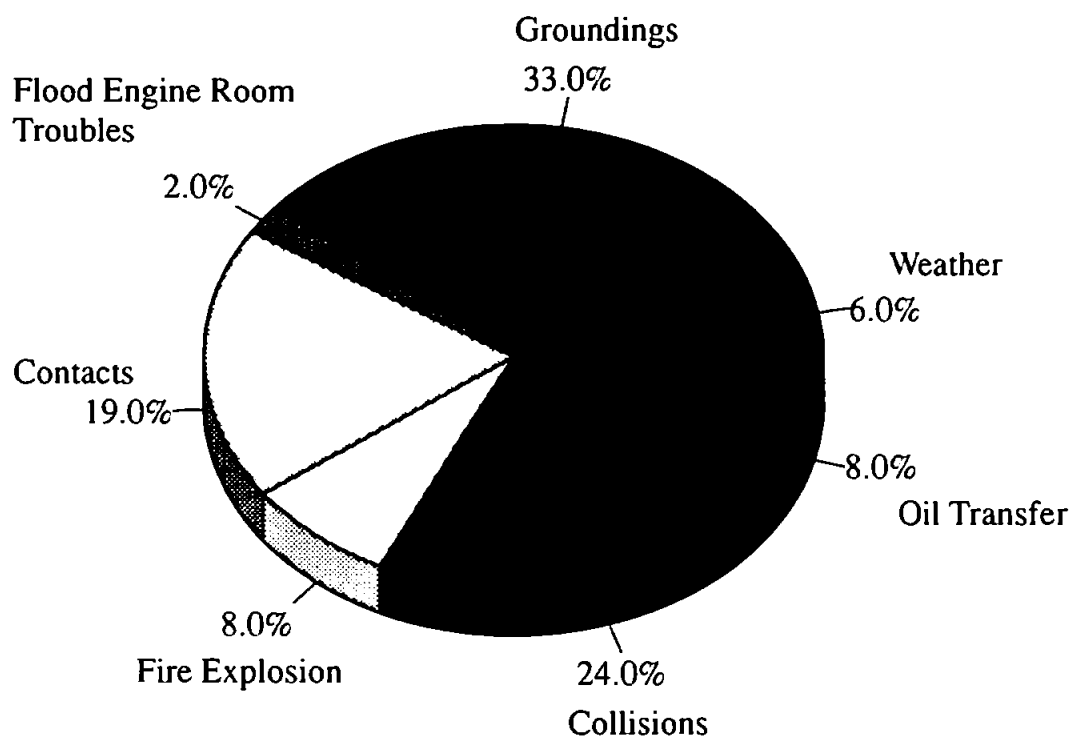


Figure 1.2 Causes of oil spills in the marine environment (Doerffer, 1992).

effectiveness of the clean-up effort (Dipper, 1991). Reports of studies on some of the coastal and marine consequences of the 1991 Gulf War which were undertaken during the 1992 Mt Mitchell cruise have been recently published (Price and Robinson, 1993). This special issue of the Marine Pollution Bulletin reviewed the impact of the massive oil spillage on the marine environment of the region.

In view of the number of oil spills occurring both on inland waters and the open seas, it is essential that the fate of petroleum and its products on the environment be thoroughly studied and understood in order to assess accurately the ecological effects. It has been reported that when spills of crude oil occur in an aquatic environment, even after clean-up, water soluble components may remain and continue to exert deleterious effects on the environment and can potentially pose risks to human lives through accumulation of the toxins in the food chain (IMCO/FAO/UNESCO/WHO/IAEA/UN, 1977).

Crude oils vary widely in their physical and chemical composition depending upon their geochemical derivation. However, all crude oils consist of a complex mixture of compounds comprised mainly of hydrocarbons. The hydrocarbon components of crude oil consist of straight and branched chain alkanes, cycloalkanes and aromatics. The relative content of these groups of compounds varies from oil to oil. Compounds containing oxygen, nitrogen, sulphur and various metals (Ni, V, Fe, Zn, Cu, U) are also present in crude oil (Tissot and Welte, 1984).

The chemistry of crude oil in relation to oil spillage at sea has been extensively reviewed (Dean, 1968; Smith, 1972; Nounou, 1980; Robotham and Gill, 1989). Immediately after the release of crude oil into the sea a number of biotic and abiotic influences begin to

change the physical and chemical composition of the oil (Figure 1.3). Evaporation enhanced by spreading processes depletes volatile components at a rate proportional to their vapour pressure. These processes start immediately on spillage and may continue for weeks resulting in the removal of between 30-50% of the total hydrocarbons (Clark and Macleod, 1977). Dissolution and evaporation are two competing processes on the overall rate of slick disappearance. The rate of dissolution of the constituent components in seawater is in proportion to their solubility (Jordan and Payne, 1980). Strong sea conditions tend to disperse the oil into the sea in the form of droplet dispersions and emulsions, both oil-in-water and water-in-oil (Berridge *et al.*, 1968). Adsorption by particulate matter and consequent sinking, or the formation of tar balls which drift and end up on shorelines are likely to be important following evaporation and other processes which increase the density of the residual oil slick (Jordan and Payne, 1980). The released oil is thus divided into three phases; a vapour phase, a dispersed and dissolved phase and the remaining phase of bulk oil. The dissolved phase, whose composition reflects the sea water solubilities of its individual compounds may be very different from that of the original oil and may be further altered by microbial degradation and photochemical oxidation. These processes may lead to increased toxic effects on marine life (e.g. Tilseth *et al.*, 1984; Sydnes and Burkow, 1985; Ehrhardt *et al.*, 1992).

The rates at which the different weathering processes can occur depend upon the type and quantity of oil and the amount of energy available in the environment such as wind, waves, currents, sunlight and temperature. Attempts have been made to quantify these rates (Boehm, 1987). The physical processes such as evaporation and dissolution have no direct effect upon the chemical structure of constituent hydrocarbons, but lead to a decrease in total oil concentration and the dispersal of oil throughout the ecosystem. Two of the

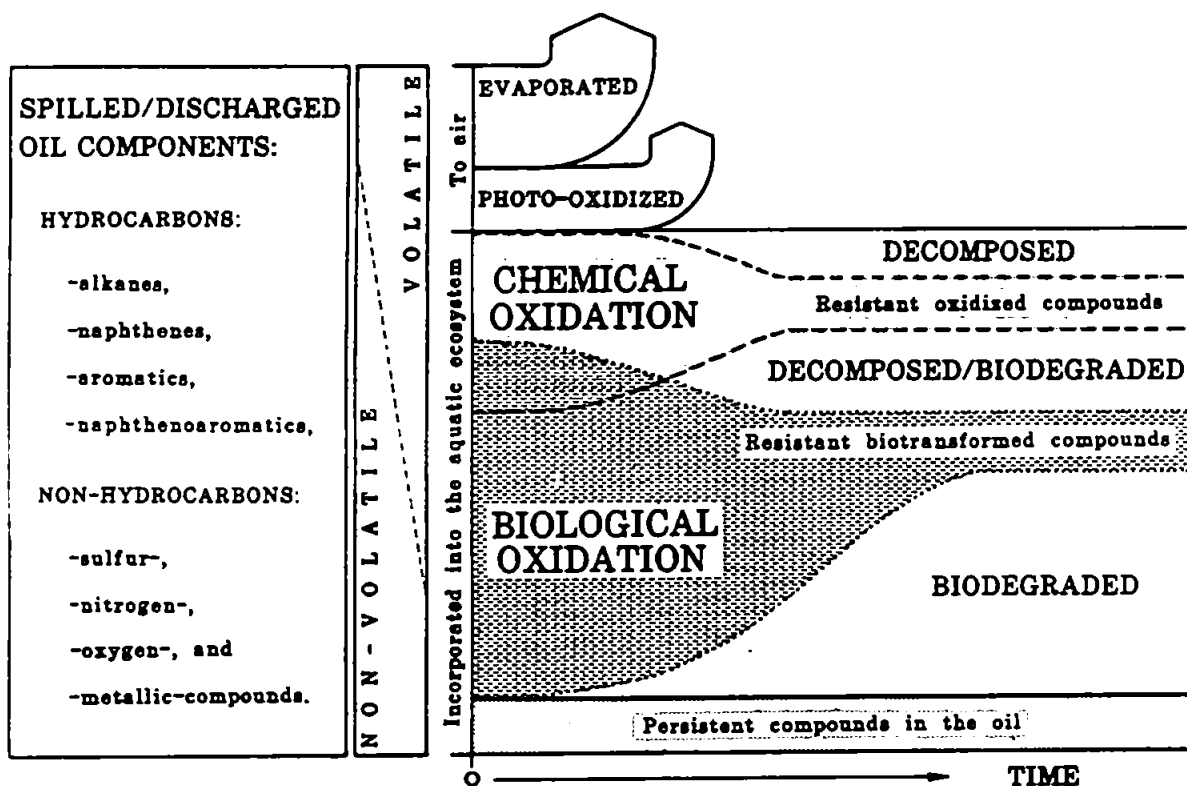


Figure 1.3 Changes in oil composition during environmental weathering of spilled/discharged oil as a result of physical, chemical and biological weathering processes (Literathy *et al.*, 1989).

primary factors affecting petroleum degradation are photooxidation (reviewed by Payne and Phillips, 1985) and biodegradation (e.g. Kennicutt, 1988, Oudot and Dutrieux, 1989). These processes may be equally important to oil breakdown, although in environments of intense solar radiation photodegradation may play the major role (Ehrhardt and DouAbul, 1989; Literathy *et al.*, 1989; Ehrhardt and Burns, 1993).

A major problem in studying the fate of oil degradation in the aquatic environment is how to design experiments which will accurately simulate the environment and provide realistic measurements of these processes at sea. Several attempts have been made to undertake 'fate of oil' studies directly in the environment (reviewed by National Academy of Science (NAS), 1985). Such work is complicated by the number of interacting processes which take place simultaneously and which make data interpretation very difficult. Laboratory simulations have provided much useful information about the loss and degradation of oil under a variety of conditions. Under these conditions many of the environmental parameters which affect spilled oil may be controlled, thereby limiting the dynamic complexity and making data interpretation somewhat easier (e.g. Burwood and Speers, 1974; Riley *et al.*, 1980-1981, Sydnese *et al.*, 1985a, 1985b; Daling and Brandvik, 1992). Nevertheless, laboratory results can sometimes be misleading, particularly when unrealistic environmental conditions are employed.

With reference to photodegradation, Zika (1981) emphasised that ".... caution must be used in extrapolating the results of studies where considerable deviation from prevailing natural conditions have been employed. Extensive liberties have been taken with regard to this point with the result that the literature now contains many references which were done under the guise of environmental photochemistry, which probably have little or no

relevance with regard to the natural environment".

From a photochemical viewpoint, crude oils are very complex mixtures whose oxidation kinetics can be influenced by components of different photophysical properties or radical reactivities. A detailed analysis of the photooxidation of crude oil is therefore complicated, but useful information can be derived from much simplified mixtures of differing composition or the use of model compounds (e.g. Zepp and Schlotzhauer, 1979; ThomINETTE and Verdu, 1984a; Fukuda *et al.*, 1988). During photooxidation of petroleum components the different conversion products which usually comprise oxygenated compounds may alter the effects of the oil on the aquatic ecosystem (e.g. Patel *et al.*, 1979; SydnE and Burkow, 1985). A better understanding of photochemical aspects of the transformation/degradation process is required with particular emphasis given to the water soluble fraction and the resultant formation of toxic products.

There are a number of problems involved in conducting photodegradation experiments. In particular the use of inappropriate sources of irradiation which are unable to maintain stable light intensity and constant temperature during the course of the experiments is to be avoided. A methodology which allows reproducible sampling, good recovery of samples, and accurate quantification is essential. Consideration of experiments designed for the quantification of degradation rates for other environmental pollutants, such as pesticides, may prove valuable (Parker and Leahey, 1988).

1.2 Aims of the Research

There has been limited research into the role of the photodegradation process operating on

oil spills at sea. These processes were for many years regarded as relatively unimportant. More recent research suggests that in certain environments photodegradation plays a significant and important role in the fate of an oil spill. However, many previous studies, have utilised inappropriate radiation conditions which do not effectively simulate natural solar radiation.

To this end, this work attempted to quantify the rates of photodecomposition of the components of the seawater-soluble fraction of Kuwait crude oil (SWSF) under simulated artificial sunlight using a 1.8 kW xenon lamp. An experimental system was developed for the quantitative evaluation of the rate of photodegradation of the components of SWSF under realistic and well controlled environmental conditions.

The specific aims of this research were to:

1. Prepare a representative, homogeneous solution of SWSF of Kuwait crude oil and to monitor the dissolution by ultraviolet-fluorescence (UVF) spectroscopy and dissolved organic carbon (DOC) methods.
2. To undertake a detailed characterisation of the components of the SWSF and the same components in the fresh oil by gas chromatography-mass spectrometry (GC-MS).
3. To construct an irradiation system, to photodegrade a model SWSF compound and to undertake quantitative characterisation of the photoproducts.
4. To photodegrade the characterised SWSF and determine the rates of degradation of the individual components.

CHAPTER TWO

CHAPTER TWO

PREPARATION OF A SEAWATER SOLUBLE FRACTION OF A KUWAIT CRUDE OIL

2.1 Introduction

In terms of the environmental and ecological effects of oil pollution, the degree to which crude oil components dissolve in seawater is very important. For example, it has been established that it is the dissolved rather than the emulsified or the adsorbed fractions of oil which are acutely toxic to marine life. The reason for this is that the dissolved fraction is readily ingested by organisms at the lower end of the food chain and concentrates and accumulates in organisms at higher trophic levels (Robotham and Gill, 1989).

Although the solubility of many crude oils in seawater is low being at most 30 mg L⁻¹ seawater at 22 ± 2 °C (Shiu *et al.*, 1990), the volume of seawater is much greater than the volume of oil in most oil spills and, consequently, significant amounts of oil can still be dissolved.

Some of the more polar non-hydrocarbons as well as the low molecular weight hydrocarbons found in crude oil will dissolve readily in seawater. The rate of dissolution for the components of a petroleum slick depends on complex interactions between properties inherent to the oil (i.e. composition and relative abundance of the components, specific gravity and viscosity) and the physical-chemical properties of the prevailing environment (e.g. sea state, salinity, temperature, pH). Some dissolution begins

immediately the oil comes into contact with seawater, but there are also longer-term effects. For example, photo- and biodegradation of the original oil constituents progressively produces increasing numbers of more polar compounds some of which are more soluble in seawater than the precursor hydrocarbons (Larson *et al.*, 1977).

Spreading of the oil increases the contact area between the slick and seawater and is likely to increase the dissolution of water soluble components (International Tanker Owners Pollution Federation (ITOPF), 1987). In contrast, under some conditions, loss of highly soluble and volatile aromatic hydrocarbons from an oil slick through dissolution in seawater may be minimal compared to the losses due to evaporation (Doerffer, 1992) and, with time, the rate of dissolution may be further decreased as the oil becomes depleted in its lighter, more soluble components by evaporation (Figure 2.1).

Any experimental study of crude oil dissolution in water should take into consideration at least three factors: chemical factors, environmental factors and experimental factors.

2.1.1 Chemical Factors

Of those compounds of low molecular weight which occur commonly in crude oil, aromatic hydrocarbons have the greatest solubility. Small amounts of high molecular weight polar compounds may also dissolve. These are often collectively referred to as the water soluble fraction (WSF) or SWSF if dissolved in seawater.

McAuliffe (1966) first documented the solubility of a number of hydrocarbons in both fresh and salt water and suggested that for each homologous series of hydrocarbons, the

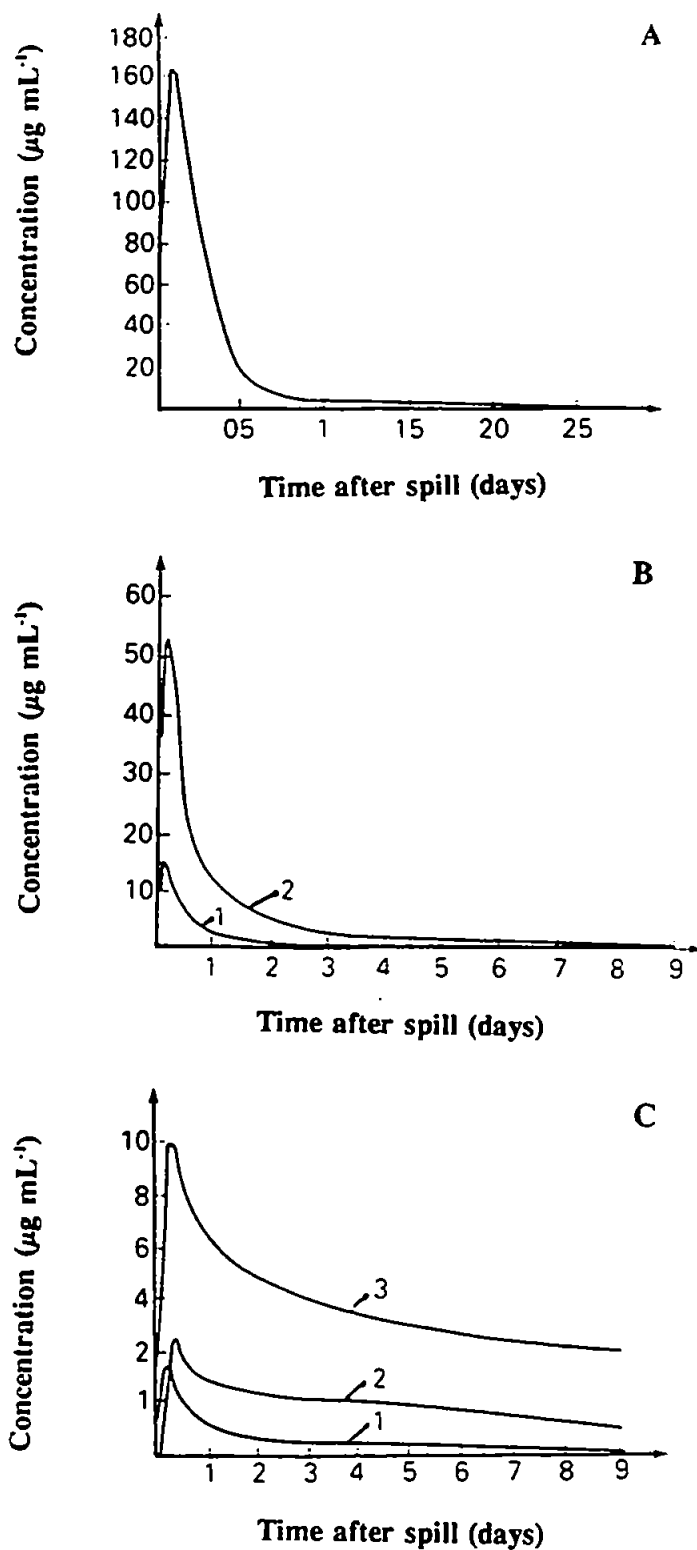


Figure 2.1 Concentration of dissolved aromatic components in a water column obtained from a wave tank experiment as a function of weathering time: (A) toluene; (B) 1 ethylbenzene; 2 1,4-dimethylbenzene; (C) 1 *n*-propylbenzene; 2 methylnaphthalenes; 3 C_2 -naphthalenes (Doerffer, 1992).

logarithm of the solubility in water at room temperature of the pure hydrocarbons was a linear function of the hydrocarbon structure. The solubility of the main classes of hydrocarbon decreases in the order: aromatics > cycloalkanes > isoalkanes > *n*-alkanes. These solubility characteristics were confirmed by Ogawa *et al.* (1980) from a study of the physical and chemical characteristics of crude petroleum and its derivatives in seawater.

Aromatic compounds are the main classes of hydrocarbon found in the SWSF and their solubility decreases with increasing number of rings in the molecule. The presence of alkyl groups on aromatic compounds generally results in a decrease in the solubility according to the increase in the molar volume; the larger the alkyl substituent, the greater the decrease in solubility. For example, the solubility of alkylated benzenes decreases in the order: benzene > ethylbenzene > isopropylbenzene (Jordan and Payne, 1980).

Furthermore, the number of alkyl substituents affects the solubility in a similar way: naphthalene > 1-methylnaphthalene > 1,5-dimethylnaphthalene. The solubility data of these and other petroleum hydrocarbons in water are listed in Table 2.1.

The solubility of pure hydrocarbons in water however will not be the same as that in a competitive two-phase, water-oil system. The dissolution of individual components from an oil slick is controlled by the mole fraction of each component in the slick and the oil/water partition coefficient, but not by pure component solubilities. The partition coefficient for distribution between the aqueous and oil phases is defined as the ratio of the equilibrium concentration of the component in the oil phase to that in the water phase, and the value is characteristic of the composition of both phases and temperature (Doerffer, 1992). It is not always possible to determine these dissolutions because of the

Table 2.1 Solubility of petroleum hydrocarbons in water.

Compound	Carbon number	Solubility* (ppm)
<u>Alkanes</u>		
Methane	1	24
Ethane	2	60
Propane	3	62
<i>n</i> -Butane	4	61
<i>n</i> -Pentane	5	39
<i>n</i> -Hexane	6	9.5
2-Methylpentane	6	13.8
3-Methylpentane	6	12.8
2,2-Dimethylbutane	6	18.4
<i>n</i> -Heptane	7	2.9
<i>n</i> -Octane	8	0.66
<i>n</i> -Nonane	9	0.220
<i>n</i> -Decane	10	0.052
<i>n</i> -Undecane	11	0.0041
<i>n</i> -Dodecane	12	0.0037
		0.0029 (SW)
<i>n</i> -Tetradecane	14	0.0022
		0.0017 (SW)
<i>n</i> -Hexadecane	16	0.0009
		0.0004 (SW)
<i>n</i> -Octadecane	18	0.0021
		0.0008 (SW)
<i>n</i> -Eicosane	20	0.0019
		0.0008 (SW)
<i>n</i> -Hexacosane	26	0.0017
		0.0001 (SW)
<i>n</i> -Triacontane	30	0.002
<i>n</i> -Heptacontane	70	10 ⁻³ ^b
<u>Cycloalkanes</u>		
Cyclopentane	5	156
Cyclohexane	6	55
Cycloheptane	7	30
Cyclooctane	8	7.9
<u>Aromatics</u>		
Benzene	6	1780
Toluene	7	515
<i>o</i> -Xylene	8	175
Ethylbenzene	8	152
1,2,4-Trimethylbenzene	9	57
<i>iso</i> -Propylbenzene	9	50
Naphthalene	10	31.3
		22.0 (SW)
1-Methylnaphthalene	11	25.8
2-Methylnaphthalene	11	24.6
2-Ethylnaphthalene	12	8.00
1,5-Dimethylnaphthalene	12	2.74
2,3-Dimethylnaphthalene	12	1.99
2,6-Dimethylnaphthalene	12	1.30
Biphenyl	12	7.45
		4.76 (SW)
Acenaphthene	12	3.47
Phenanthrene	14	1.07
		0.71 (SW)
Anthracene	14	0.075
Chrysene	18	0.002

^a In distilled water, except where noted by (SW), indicating filtered seawater, usually corrected to a salinity of 35‰ (parts per thousand); ppm = parts per million-microgram per gram.

^b Extrapolated

Source: Robotham and Gill (1989)

difficulties involved in analyzing dilute concentrations of the components (Harrison *et al.*, 1975).

2.1.2 Environmental Factors

Environmental factors which directly influence the solubility of oil components include temperature and salinity. Table 2.1 shows relationship between salinity and hydrocarbon solubility for both aliphatic and aromatic components. An approximate decrease of 30% solubility for paraffins was observed between freshwater and seawater. Mochalova *et al.* (1986) found that the concentration of polar hydrocarbons was inversely proportional to the salinity of the seawater when they were in equilibrium distribution between the petroleum film and the water phase.

Gearing and Gearing (1982) found that the process of oil partitioning into the water column was also sensitive to temperature. However, Rossi and Thomas (1981) pointed out that seawaters at different temperatures will only vary moderately in their ability to solubilise aromatic hydrocarbons, particularly when nominal concentrations are near the solubility limit.

Other environmental factors which enhance the emulsification of the oil can also act indirectly to increase the rate of dissolution of water soluble oil components, by increasing the surface area between the aqueous and non-aqueous phase. Artificial detergents and natural dispersants (e.g. lipids and humic acids) as well as agitation of the water by wind and wave action can also lead to the formation of emulsions (Robotham and Gill, 1989). The formation of small droplets increases the rate of dissolution and the rate of chemical,

photochemical and biochemical attack.

2.1.3 Experimental Factors

Published data on solubility are not always comparable and do not always allow generalisations regarding the solubility of the various petroleum hydrocarbons in natural seawater to be made. This is because such data have been usually obtained in laboratory tests involving a variety of experimental conditions, petroleum substances, and seawater compositions.

Variations in experimental parameters have included: type, degree and duration of mixing of petroleum and seawater; the ratio of petroleum to water; filtration of the oil solution (type of filter, pore diameter, and filtering rate or pressure); and the analytical methods used to determine oil SWSF concentration. Studies which have investigated these experimental parameters are reviewed in the following section. The petroleum substances have varied as to type (crude petroleum or refined products), fraction (whole oil, weathered residue, or distillation fraction), and source. The composition of seawater has varied in terms of salinity, pH, source (estuarine, coastal, open-ocean, artificial), and presumably, content of naturally-occurring organic matter (although this has rarely been mentioned).

Several methods have been proposed for preparing seawater extracts of petroleum. "Ideal" SWSFs for the study of the effects of crude oil in the marine environment should represent situations that can occur in the environment as a result of an accidental discharge or from chronic inputs. However, the natural environment has a distribution of energy (e.g. winds,

waves, tides, heat, light) that is virtually impossible to duplicate in the laboratory. Nevertheless, laboratory simulations can provide some degree of understanding of the partitioning of petroleum components.

An oil spill in water may ultimately be found in any or all of the following phases: as a surface film (i.e an oil slick); dispersed and emulsified; adsorbed onto particulate matter, or as a true water soluble fraction.

Laboratory simulations have produced extracts of petroleum by different mixing methods ranging from gentle stirring to turbulent mixing (see National Academy of Sciences (NAS), 1985 for review). Researchers have prepared dispersions (droplet dispersions, colloidal dispersions and oil-in-water emulsions) by shaking, blending, ultrasonically emulsifying, passing through baffle plates, and turbulent mixing in a water jet. Single phase (WSF) extracts have been produced by slow stirring and flow-through systems; and surface slick solutions have been prepared in both open chambers and in tanks.

In general, turbulence induced by shaking has a pronounced effect on the observed concentration. The greater the turbulence the greater the concentrations, and the hydrocarbon composition has usually been assumed to resemble that of the parent oil (e.g. Boylan and Tripp, 1971; Gordon *et al.*, 1973). However, oil solutions of this nature are unstable and concentration will vary with time after separation due to physical factors, such as droplet size, temperature and the presence of air or vapour space above the dispersion. Anderson *et al.* (1974) found that the total concentration of hydrocarbons in the water dispersion of gently aerated South Louisiana crude oil decreased by almost 90% within 24 hours.

In addition to mixing, other experimental factors such as duration of treatment, temperature, light, and microbial activity will influence the physical nature and chemical composition of the extract. A standard procedure for providing an oil extract is not yet available and the composition of extracts that have been produced vary accordingly.

The WSFs which are prepared by slow stirring techniques produce homogeneous single-phase solutions, which are highly reproducible and relatively stable oil-in-water mixtures if mixing conditions are carefully standardised. Boylan and Tripp (1971) and Shaw and Reidy (1979), have shown that slow stirring with no formation of visible oil droplets gives an aqueous phase that is highly enriched in phenols and aromatic hydrocarbons, relative to the composition of the oil. In contrast, vigorous shaking gives extensive emulsification and a composition very similar to that of the original oil (Figure 2.2).

A SWSF is a homogeneous and a relatively stable oil-in-water mixture that is a simplified oil extract, when compared to the parent crude oil. In this study this method was chosen in order to determine quantitatively the photodegradation kinetics of the hydrocarbons present in solution under controlled conditions.

The concentration of mono- and diaromatic components make an important contribution to the acute toxicity of water-soluble hydrocarbons (e.g. Caldwell *et al.*, 1977; Clement *et al.*, 1980). It was therefore of interest to study their photochemical fate in association with this seawater soluble extract.

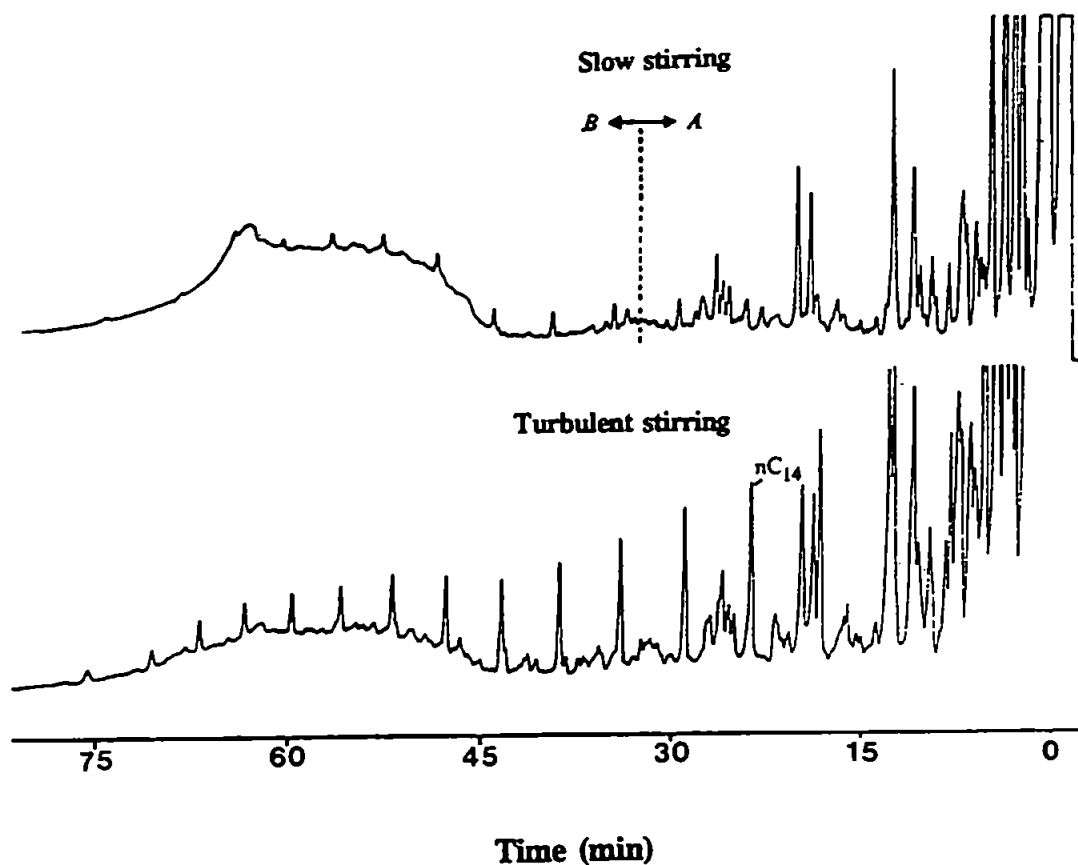


Figure 2.2 Gas chromatograms of seawater extracts of Kuwait crude oil. Slow stirring conditions: (A) benzene and naphthalene region; (B) polar aromatic region. Turbulent stirring conditions: increase in chromatogram complexity is due to presence of saturated hydrocarbons (Boylan and Tripp, 1971).

2.2 Literature Review of the Preparation of Seawater-Soluble Fractions of Crude Oil

Several laboratory simulation studies have described the preparation of the SWSFs of crude oil (see National Academy of Sciences (NAS), 1985 for review). The solubilities reported vary according to a number of key factors including:

1. the composition of the oil;
2. the ratio of the volumes of oil to water which are brought into contact;
3. mixing rate and time;
4. seawater temperature, salinity and pH;
5. other effects such as: separation time, filtration, volatilisation, dilution, illumination during preparation, and flask dimensions; and
6. the method of WSF analysis.

Table 2.2 summarises some typical findings from the preceding studies and these are discussed in more detail below.

2.2.1 Effect of Oil Composition

Although SWSFs prepared from different crude oils are qualitatively similar in composition (at least for the principal compounds), the relative abundance of the soluble compounds differs according to the abundance of these compounds in the parent oil. Lockhart *et al.* (1984) analysed SWSF solutions prepared from three different types of crude oil (Kuwait, Norman Wells and Synthetic crude) by headspace and micro-extraction analysis. They showed that the maximum contribution of all types of crude oil to the

Table 2.2 Summary of selected studies on the preparation and quantification of SWSF.

Author & Year	Crude Oil Used	Oil : Water	Preparation Method	Stirring Time (hr)	Water Temperature °C	Salinity ‰	Standing Time (hr)	Method of Quantifying Total Compounds	Concentration of Total WSF $\mu\text{g mL}^{-1}$
Anderson <i>et al.</i> , 1974	South Louisiana, Kuwait	1:9	Seawater was stirred slowly with a magnetic stirbar in a 5 gallon Pyrex bottle, capped with aluminium foil to minimise evaporation. Vortex did not extend more than 25 % of the distance to the bottom of the bottle. After allowing the mixture to stand, water phase was siphoned off and utilised immediately.	20	20 \pm 2	15-20	1-6	IR, measured in CCl_4 extracts (API method no. 733-58)	South Louisiana crude = 19.8 Kuwait crude = 10.4
Burwood & Speers, 1974	Middle East, s.g (20°C) = 0.862 Sulphur (%wt) = 2.00 Wax (%wt) = 5.00	1:50	Seawater (artificial) was stirred slowly with a magnetic stirbar in a conical flask stoppered with cotton wool plugs. Water phase was withdrawn from a tap fitted to the bottom of the flask.	6 hour - 4 weeks	20 \pm 2	38	NR	UV, measured in iso-octane extracts in the region 240-280 nm, calibrated with standard solutions of benzene in iso-octane.	11-23 expressed arbitrarily in terms of benzene equivalent
Winters <i>et al.</i> , 1977	Kuwait, Venezuela, Alaska, Southern Louisiana and fuel oil.	1:8	Seawater was stirred with a magnetic stirbar in a sealed bottle, at a rate which avoided the formation of an emulsion. Water phase was removed by means of a stopcock at the base of the bottle.	24	25	NR	several minutes	Continuous liquid-liquid extraction with benzene, dried by evaporation at room temperature, then weighed. Redissolved and analysed by GC.	Not reported for the crude oils

"Continued..."

Table 2.2 "Continued"

Author & Year	Crude Oil Used	Oil : Water	Preparation Method	Stirring Time (hr)	Water Temperature °C	Salinity ‰	Standing Time (hr)	Method of Quantifying Total Compounds	Concentration of Total WSF $\mu\text{g mL}^{-1}$
Caldwell <i>et al.</i> , 1977	Cook Inlet	1:100	Method of Anderson <i>et al.</i> , 1974	20	13	29-34	3	UV, measured at 221 nm in hexane extracts.	0.0083 ± 0.0019 expressed as naphthalene equivalent
Blackman & Law, 1980	Kuwait	1:9	Seawater was stirred slowly in a glass aspirator (sizes between 5-15 L were tested), neck was closed but not sealed, oil vortex held at 25% of the water column depth. water samples were withdrawn through the aspirator tap and filtered using pressure through 0.2-0.45 μm filters.	24 - 72	19.5 ± 1.5	33.5	0-1	<p>1) UVF, measured at 310 nm excitation, 360 nm emission in solvent extracts.</p> <p>2 IR, the absorbance was measured at 2930 cm^{-1} corresponding to the stretching frequency of C-H bands in aliphatic CH_2- groups.</p> <p>Quantification in both methods was with respect to the fresh crude oil used to prepare the WSF.</p>	<p>0.5 - 1.00 oil equivalent</p> <p>1.1 - 5.8 oil equivalent</p>

"Continued..."

Table 2.2 "Continued"

Author & Year	Crude Oil Used	Oil : Water	Preparation Method	Stirring Time (hr)	Water Temperature °C	Salinity ‰	Standing Time (hr)	Method of Quantifying Total Compounds	Concentration of Total WSF $\mu\text{g mL}^{-1}$
Busdosh, 1981	Prudhoe Bay	1:1000,000 1:100,000 1:10,000 1:1000 1:100 1:10	Seawater was stirred with a teflon-coated magnetic stirbar. After allowing the mixture to stand, the WSF was siphoned from 5 cm below slick.		5	27	12	UVF, measured in DCM extracts at 405 nm excitation, 450 nm emission (the maximum wavelengths). Quantification was made with calibration curve prepared from the whole oil.	1:10 ⁶ gave 0.20-0.23 1:10 ⁵ gave 0.24-0.26 1:10 ⁴ gave 2.90-3.50 1:10 ³ gave 3.20-3.60 1:10 ² gave 3.80-4.10 1:10 gave 4.40-5.20
Pearson <i>et al.</i> , 1981	Prudhoe Bay	1:9	Seawater was stirred with a magnetic stirrer in a glass carboy sealed with rubber stopper wrapped in aluminium foil at a rate that produced a 2.0 to 2.5 cm vortex. After settling, seawater fractions were siphoned off, then filtered using pressure through a 0.4 μm membrane filter.	20	20	24	4	Helium equilibration GC for the monoaromatics and by GC for other hydrocarbons present after acidifying the WSF and extraction with hexane.	24.05

"Continued..."

Table 2.2 "Continued"

Author & Year	Crude Oil Used	Oil : Water	Preparation Method	Stirring Time (hr)	Water Temperature °C	Salinity ‰	Standing Time (hr)	Method of Quantifying Total Compounds	Concentration of Total WSF $\mu\text{g mL}^{-1}$
Østgaard and Jensen, 1983a	Ekofisk	1:20	Sterilised seawater (autoclaved) was stirred at voltage (120-170 V) with a standard magnetic stirrer, held in a 5 L glass bottle closed with a silicone stopper. Samples were collected in sterilised brown flasks by pumping through a glass/silicon rubber tubing located below the level of the oil layer. The flasks were completely filled before closing.	10 days	14	25	NR	<p>By direct fluorescence analysis at excitation 230 & 265 nm and at emission 300 & 335 nm for naphthalene and phenol fractions, respectively.</p> <p>2) Head space analysis of the highly volatile compounds using benzene-d_6 as internal standard.</p> <p>3) Extracted with DCM for the less volatile components, dried with Na_2SO_4 and concentrated to 300 μL, then analysed with GC standardised with known amount of the crude oil.</p>	<p>Results of UVF were expressed in fluorescence intensity units: $1,200 \pm 4$ at $\lambda_{\text{ex/cm}} = 230/335$ nm 806 ± 5 at $\lambda_{\text{ex/cm}} = 265/300$ nm.</p> <p>9.85</p> <p>C_{17} fraction was 4.6</p>

"Continued..."

Table 2.2 "Continued"

Author & Year	Crude Oil Used	Oil : Water	Preparation Method	Stirring Time (hr)	Water Temperature °C	Salinity ‰	Standing Time (hr)	Method of Quantifying Total Compounds	Concentration of Total WSF $\mu\text{g mL}^{-1}$
Lockhart <i>et al.</i> , 1984	Norman Wells, Kuwait,	1:20 to 1:1000	Seawater was stirred vigorously on a magnetic stirrer. After allowing the mixture to stand, SWSFs was drained from the bottom of the mixing container.	2	NR	NR	48	GC using head space analysis for the most volatile materials and solvent extraction for less volatile materials. Quantification was by reference to <i>n</i> -decylbenzene internal standard.	Norman Wells = 60.1 Kuwait = 35.3
Michel & Case, 1984	Platform Holly, Monterey Formation	1:25	The head space above the oil layer contained in a 2 L glass aspirator was flushed with N_2 and tightly capped. The seawater was stirred with 40 mm stirbar. Vortex of 7 mm deep was formed. After allowing the mixture to stand, SWSF was drained through the stopcock into clean containers with no head space.	48	NR	NR	1	Principal volatile constituents of SWSFs were quantified by GC using a gas/tenax trap technique optimised for the recovery of benzene.	16.3 (for benzene, toluene, ethylbenzene and xylene)

"Continued..."

Table 2.2 "Continued"

Author & Year	Crude Oil Used	Oil : Water	Preparation Method	Stirring Time (hr)	Water Temperature °C	Salinity ‰	Standing Time (hr)	Method of Quantifying Total Compounds	Concentration of Total WSF $\mu\text{g mL}^{-1}$
Maher, 1986	Barrow, Cooper, Arabian Light, Qatar	1-3 g oil:400 mL seawater. Specific ration is not reported for each oil.	Seawater (filtered and sterilised by steaming) was stirred with a magnetic stirbar which produced 0.5 cm vortex. SWSF was collected through a tube located below the oil layer. SWSF samples were measured unfiltered and filtered using 0.45-1.0 μm filters.	24-72	20	NR	10 - 15 minutes	UVF measured at 300 nm excitation, maximum emission wavelengths were determined by scanning between 310-390 nm. Quantification was made with reference to the respective oils.	Results were as minimum (0.45 μm filtrates) - maximum (unfiltered): Barrow = 0.28-3.1 Cooper = 0.39-2.6 Arabian Light = 0.14-1.03 Qatar = 0.22-1.9
Glamuzina <i>et al.</i> , 1990	Iraq	1:9	Method of Anderson <i>et al.</i> , 1974	20	18	38	1	UV measured in hexane extracts at 221 nm, standardised with naphthalene.	0.189 expressed as naphthalene equivalent
Paine <i>et al.</i> , 1992	Hibernia	1:24	Filtered and sterilised (with ultraviolet light) seawater was stirred at constant speed with a paint stirrer powered by a mounted drill motor. The 4 L glass jar flask containing the mixture was then inverted and left to separate. The undissolved oil rose to the top, WSF was drawn from the bottom of the flask.	10	NR	NR	18	UV, measured at selected wavelengths (not given). Quantification was made from a calibration curve.	5.43 (range 3.96-6.53, SD 0.67)
Sophia & Blasubramanian, 1992	Kuwait	1:9	Method of Anderson <i>et al.</i> , 1974.	20 hr	20 \pm 2	NR	1 - 6	UVF, no details of the quantification procedure was given.	12.72

NR: Not Reported

SWSF were from the volatiles (C_1 - C_6 *n*-alkanes, benzene and toluene). However, the concentration of these volatile components varied; for example, for Kuwait crude oil it was $31 \mu\text{g mL}^{-1}$, and for Norman Wells oil it was $53 \mu\text{g mL}^{-1}$ as shown by headspace analysis. The concentration of the relatively less volatile constituents (C_2 - C_4 alkylbenzenes, naphthalene and methylnaphthalenes) in SWSF were also lower in Kuwait crude oil ($3.8 \mu\text{g mL}^{-1}$) as compared with Norman Wells crude oil ($6.7 \mu\text{g mL}^{-1}$).

On the other hand, the analysis of a SWSF prepared from Iraq crude oil using a 1:9 oil to water ratio mixture of 38 ‰ salinity, stirred for 20 h at 18 °C and allowed to separate for 1 h, showed that this fraction contained mainly aromatic hydrocarbons, particularly the monoaromatic components. The concentration of naphthalene as analysed by UV-spectroscopy was $0.189 \mu\text{g mL}^{-1}$ (Glamuzina *et al.*, 1990).

Soto *et al.* (1974) found, in agreement with the observations of other researchers, that extracts from aged (or weathered) crude oil did not show significant biological effects. This provided an indication of the role of the volatile fractions, which are the key toxic components of oil.

2.2.2 Effect of Oil to Water Ratio

The wide range of oil to water ratios used by researchers to prepare the SWSF has produced a range of concentrations of compounds. For example, Busdosh (1981) prepared a SWSF of Prudhoe Bay oil of six oil to water mixtures, ranging between 1:10⁶ and 1:10, oil to water. The actual amount of oil present in the oil-water solution was tested by UV spectrophotometry over a two week period. The results showed that the concentration of

the SWSF solutions was generally indicative of the relative amount of oil initially added. For example, an oil to water ratio of 1:10 resulted in a total concentration of 4-5 $\mu\text{g mL}^{-1}$ oil compared to 0.2-0.23 $\mu\text{g mL}^{-1}$ oil for the highest oil to water ratio of 1:10⁶.

Pearson *et al.* (1981) used an oil to water ratio of 1:9 to prepare a SWSF of Prudhoe Bay crude oil in a sealed carboy, with a stirring time of 20 h. The solution consisted predominately of monoaromatic hydrocarbons (24 $\mu\text{g mL}^{-1}$), and the di- and tri-aromatic hydrocarbons comprised only 0.7% (0.16 $\mu\text{g mL}^{-1}$) of the total hydrocarbons.

Shiu *et al.* (1990) reported alternative methods to explore the effect of oil to water ratios on the preparation of saturated crude oil solutions. In one method, oil was coated on a solid packing in a tube or column, then water was passed slowly through the tube, allowing it to become saturated. In a second method, oil was injected, using a 10 cm long needle, into an inverted sealed hypo vial completely filled with water. The vials were then placed on a shaker and mixed at low speed under temperature controlled-conditions to avoid emulsion formation. Although excellent reproducibility and minimum volatilization were reported, a long equilibration time of at least 20 days remained the main disadvantage of this method.

In the same study, the SWSF of three different crude oils (Western Sweet Mixed Blend, Prudhoe Bay crude and Southern Louisiana) were compared (**Figure 2.3**). The concentration of the dissolved components from the three oil types decreased as the oil to water ratio increased in agreement with the findings of Busdosh (1981). More interestingly however, the composition changed as the ratio changed. At low ratios (less than 1:100), it was found that 80% of the total SWSF concentration consisted of benzene, toluene,

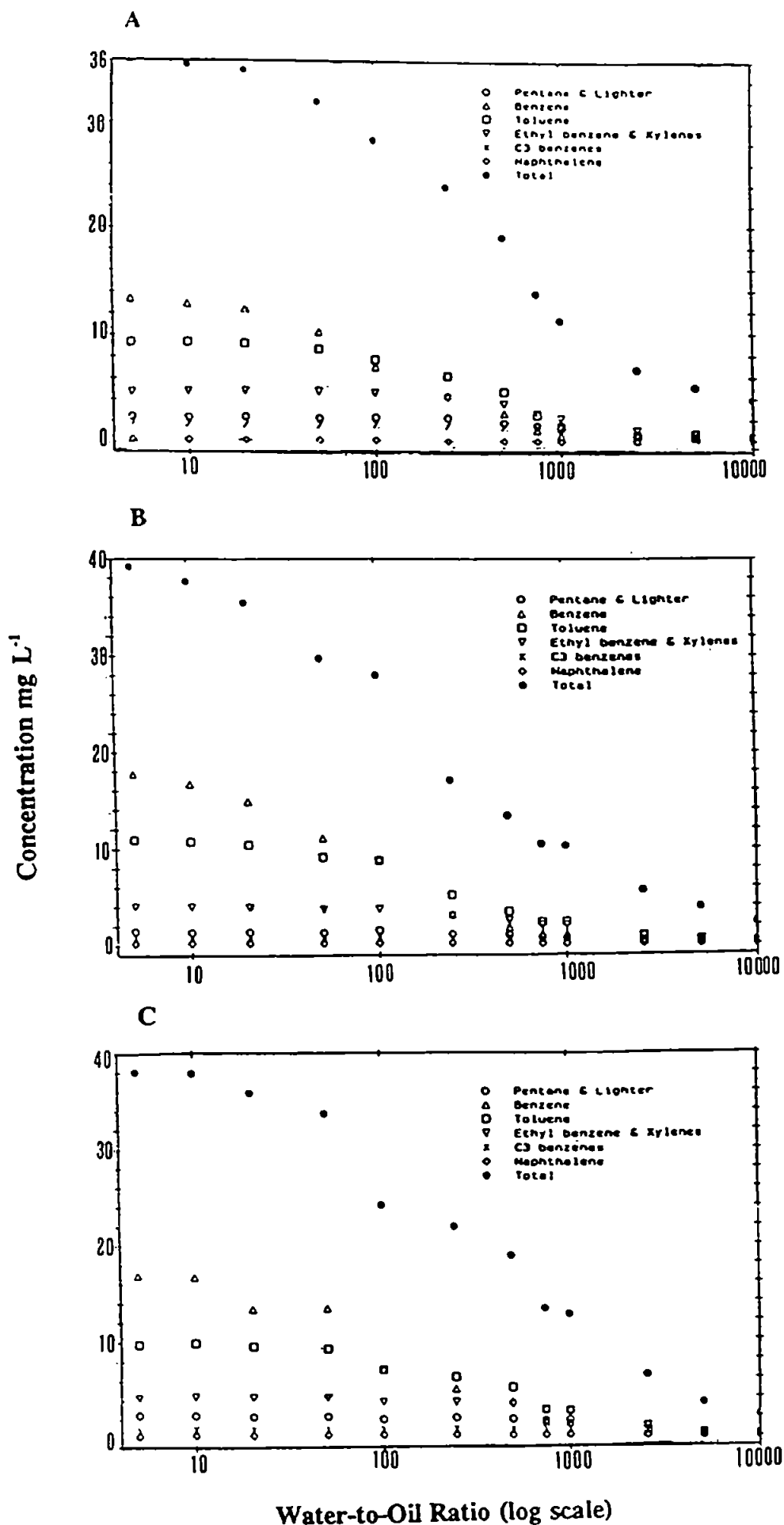


Figure 2.3 Solubility of crude oil versus water-to-oil ratio: (A) Western Sweet Mixed Blend; (B) Prudhoe Bay; (C) Southern Louisiana. Methods of preparation described in the text (Shiu *et al.*, 1990).

ethylbenzene and dimethylbenzene, with benzene as the predominant hydrocarbon. At higher ratios (1:100-1:1000) the concentration of benzene, ethylbenzene and dimethylbenzene became less significant in the total SWSF whilst toluene became the predominant component. At ratios greater than 1:1000, the total SWSF concentration decreased, and became a mixture of compounds at low concentrations. The decrease in the total SWSF concentration with increasing oil to water ratio was explained as a "depletion effect", i.e. that the oil becomes depleted in water soluble material, thus causing the apparent solubility to fall. On the other hand, the less soluble compounds such as the highly alkylated benzenes and naphthalenes were found to be less dependent upon the oil to water ratio and the concentrations remained constant over the range of oil to water ratios tested.

2.2.3 Effect of Mixing

(i) Mixing Rate

A number of studies have used turbulent mixing induced by fast stirring, shaking or ultasonication for preparing oil in seawater solutions (e.g. Gordon *et al.*, 1973; Venezia and Fossato, 1977; Lockhart *et al.*, 1984; Murray *et al.*, 1984). However, these methods have a pronounced effect on the composition and the observed concentration, the greater the mixing the greater the concentration of the oil in seawater. Concentrations between 10 and 80 $\mu\text{g mL}^{-1}$ were reported, depending on the amount and type of oil used (e.g. Anderson *et al.*, 1974; Soto *et al.*, 1974). However, since this type of solution is unstable with time due to the presence of oil droplets (Anderson *et al.*, 1974) changes in concentration will occur when the solution is left to stand.

Gentle mixing techniques have generally produced lower and more reproducible concentrations of oil in seawater (see Figure 2.2). Anderson *et al.* (1974) prepared both an oil-in-water dispersion (OWD) by turbulent mixing and SWSFs by slow stirring from a Kuwait crude oil. SWSFs prepared from an oil to water ratio of 1:9 produced a total hydrocarbon concentration of 10.4 mg L^{-1} , whereas 30 mg L^{-1} was determined from 1000 mg L^{-1} OWD. SWSF was prepared with approximately 100 times higher ratio than that used for OWD preparation but resulted in a lower total hydrocarbon concentration. These results are supported by the findings of other researchers.

Sophia and Blasubramanian (1992) used the slow stirring method of Anderson *et al.* (1974) to prepare a SWSF of Kuwait crude oil (1:9, oil to water) and found that the total hydrocarbon concentration was $12.7 \text{ } \mu\text{g mL}^{-1}$ using fluorescence measurements.

Østgaard *et al.* (1983b) stirred Ekofisk crude oil (1:20 oil to water) gently for 21 hours in a closed glass bottle to prevent evaporation. Using headspace analysis the total volatiles were $9.9 \text{ } \mu\text{g mL}^{-1}$ and using extraction and GC of "the C_{7+} fraction", $4.6 \text{ } \mu\text{g mL}^{-1}$.

(ii) Mixing Time

Blackman and Law (1980) prepared extracts by stirring separate batches of oil and water for different periods of time. Their results showed that 20 hours, as reported by Anderson *et al.* (1974) was insufficient to produce a saturated extract and that greater than 40 hours stirring time did not significantly increase the aromatic hydrocarbon content. They concluded that a stirring time of 24-30 hours seemed optimal for the preparation of saturated extracts. Furthermore, their examination of synchronous UVF spectra showed an increase in response with increasing time at 325 nm relative to that at 290 nm,

indicating a change with time in the aromatic hydrocarbon composition of the extracts. Østgaard and Jensen (1983b) showed that these wavelengths are indicative of naphthalenes and phenols.

Maher (1986), examined the effect of mixing time by stirring separate batches of crude oils and seawater for different periods of time. The aromatic hydrocarbon concentrations of the unfiltered aqueous phase gradually increased over 24-48 hours for all oil types after which the concentration decreased. However, the concentration of the 0.45 μm filtered solutions remained constant which suggests oil droplets may be contributing to the aqueous extracts over the time of stirring.

Kennish and French (1984) prepared an extract of Prudhoe Bay crude oil WSF in distilled water adjusted to pH 8, with slow stirring for 4 days. Equilibration time was found to be approximately 2 days by monitoring with UV, but the system was allowed to stir for 4 days to reach equilibration for all compounds.

2.2.4 Effect of Water Temperature, Salinity and pH

Gelder-Ottway (1976) reported that the amount of oil which went into solution increased when the temperature of seawater was increased beneath a layer of a Russian crude oil.

Lee and Craig (1974) used distilled water and 3.5% sodium chloride in distilled water to simulate seawater to prepare SWSF solutions. They noted that salt water had less aromatic hydrocarbons in its extract than distilled water only. The relative amount reported for benzene, ethylbenzene, 1,2,4- and 1,2,3-trimethylbenzene in Arabian crude oil extract

were 32%, 23%, 22%, and 12% respectively; less than their relative amounts in distilled water extracts. Similar decreases in relative amounts were also observed for African and Venezuelan crude oils studied under the same conditions.

Shiu *et al.* (1990) studied the effects of temperature and salinity on the solubility of Norman Wells and other crude oils. The aqueous solubility was determined in distilled and salt water (prepared with sodium chloride) at 5°C, 20 °C and 22 ± 2 °C. The concentrations measured by purge-and-trap GC were 30, 33 and 33.5 mg L⁻¹ for the temperatures, respectively, in distilled water. In seawater the solubility was 25.5 mg L⁻¹ at 5°C and 20 mg L⁻¹ at 22 ± 2 °C. The change in solubility was more obvious between salt water and distilled water than that induced by temperature.

Glamuzina *et al.* (1990) used a Mediterranean seawater of 38 ‰ salinity and an oil to water ratio 1:9 to prepare a stock solution of SWSF by slow stirring. The only concentration reported was that of naphthalene which was 0.189 mg L⁻¹ as measured by UV.

Winters *et al.* (1976) attributed the higher content of the phenolic compounds in the seawater soluble fraction prepared from Montana and Baytown fuel oils to the higher pH of the seawater compared to the distilled water preparation.

2.2.5 Effect of Separation Time

If carried out at low stirring speeds the SWSF should be stable and standing time may not be required, provided that the system is kept closed to prevent evaporation. This is

supported by the work of Blackman and Law (1980) and Østgaard *et al.* (1984) who noted little change in oil concentration during the first 5 hours of standing time.

However, Anderson *et al.* (1974), who were among the first to introduce a slow stirring technique for the preparation of WSF, used a 1 hr separation time. Researchers using the method of Anderson *et al.* (1974), have therefore also adopted a customary 1 hour standing time (e.g. Glamuzina *et al.*, 1990; Sophia and Blasubramanian, 1992).

Maher (1986) found that a 10-15 min standing time was sufficient to obtain reproducible concentrations of aromatic hydrocarbons in the aqueous phase of dissolved crude oils.

2.2.6 Changes Due to Filtration

Blackman and Law (1980) used filter paper of two different diameters to examine SWSF solutions. Their results showed little evidence of any increase in adsorption of aromatic hydrocarbons by increasing filter size but the variability of the aliphatic hydrocarbon concentration increased. Filtration through a pore size of 0.45 μm showed similar variability with aliphatic hydrocarbon concentration, which suggests that the aliphatic components may be present in droplet form in the oil water extract.

Maher (1986) also examined the effect of filtration on the concentration of aromatic hydrocarbons in four crude oil extracts prepared according to the slow stirring method of Anderson *et al.* (1974). He found that the aromatic hydrocarbon concentration of water soluble extracts progressively decreased by decreasing filtration pore size, indicating that oil droplets contributed to the aromatic hydrocarbons of the SWSFs.

2.2.7 Changes Due to Volatilisation

Paine *et al.* (1992) reported changes in total hydrocarbon concentration of the SWSF of Hibernia crude oil with time. The concentration dropped from $5.5 \mu\text{g mL}^{-1}$ to $1.5 \mu\text{g mL}^{-1}$ in 22 days after mixing. The solution was stored in beakers capped with aluminium foil. Similarly, Busdosh (1981) reported a decrease in total hydrocarbon concentration of the SWSF by at least half when kept in open trays for two weeks.

2.2.8 Effect of Dilution

SWSFs are usually prepared as stock solutions and different dilutions may be made by diluting the stock with fresh seawater (Glamuzina *et al.*, 1990). However, measurements of the total hydrocarbon concentration of the diluted SWSF solution are often not taken, and the concentration is calculated from the dilution factor made from the stock. Such assumptions may not be well founded.

Blackman and Law (1980) tested the reproducibility of dilution in saturated oil extracts after filtering through a $0.45 \mu\text{m}$ membrane. The neat filtrate was serially diluted with $1.2 \mu\text{m}$ filtered seawater, and the concentrations were measured by UVF. The dilutions of the neat filtrate gave lower than predicted concentration of aromatic hydrocarbons. These results were thought to be due to the presence of particulates in the diluting water (filtered only to $1.2 \mu\text{m}$) which could sweep aromatics from solution followed by adsorption to the container wall.

2.2.9 Effect of Illumination During Preparation

Østgaard and Jensen (1983a) found that light intensity influenced the preparation of the SWSF. The fluorescence level of the SWSF of Ekofisk crude oil prepared by slow stirring under normal indoor light was found to be unstable with time during a 3 week experiment. Subsequently, in order to achieve equilibrated solutions, stirring was carried out in complete darkness.

2.2.10 Effect of Flask Dimensions

Blackman and Law (1980) tested the effect of three sizes of aspirator, with varying capacity, diameters and depths of water and oil on the concentration of SWSF solutions prepared by slow stirring. Although larger internal dimensions allowed greater contact between oil and water, no significant difference was found in the aromatic hydrocarbon concentration between extracts from the three sizes of aspirator, within the variability of the methods of preparation, extraction and analysis used.

2.2.11 Methods for Analysing WSFs

Some of the analytical techniques used for determining the oil content of the SWSF solutions were shown in Table 2.2. When dealing with complex mixtures such as oil in seawater, the oil solution may be monitored by using one of the simple and rapid methods such as infrared spectroscopy (IR), ultraviolet spectrophotometry (UV), fluorescence spectrophotometry (UVF) or gas chromatography (GC), depending on the specific purpose of the analysis. However, no single method will quantify all the components in water after

an oil spill, and the success of using several complementary analytical methods has recently been emphasised (Burns, 1993).

Infrared Spectroscopy

Infrared spectroscopy is normally used to measure the saturated hydrocarbon content of a solution, but not the aromatic hydrocarbon content (e.g. Anderson *et al.*, 1974). For example, Blackman and Law (1980) used this technique to measure the concentration of saturated hydrocarbons of SWSFs of Kuwait crude oil. The absorbance of the extracted material was measured at 2930 cm^{-1} , corresponding to the C-H stretching frequency of CH , CH_2 or CH_3 groups. Quantification was based on the response of solutions of the oil.

However, considerable difficulty may sometimes be encountered with IR analysis because of problems associated with the preparation of the standards and samples.

Ultraviolet Spectrophotometry

In this method the UV spectra of solvent extracts are measured in the range of 200-350 nm. Kennish and French (1984) monitored the equilibration time of SWSF by measuring the UV absorbance at 260 nm (the wavelength which gave maximum absorption).

Quantification of SWSF by UV was made by measuring absorbance at a selected wavelength and comparing it with the absorbance of extracts prepared from arbitrary oil standards. However, the accuracy of this method significantly depends on the choice of standard for calibration and since ultraviolet absorption is dependent on composition, it is often impractical to make up adequate standards for complex petroleum hydrocarbon samples. Consequently, UV is usually measured in equivalents of a specific compound,

such as naphthalene (e.g. Caldwell *et al.*, 1977; Glamuzina *et al.*, 1990). Neff and Anderson (1975) determined the concentration of the SWSFs of crude oil by measuring the absorbance maxima at 221, 224 and 228 nm corresponding to naphthalene, 2-methylnaphthalene and 2,6-dimethylnaphthalene, respectively.

Law (1990) stated that SWSFs of oil enriched in one-ring aromatic hydrocarbons show a strong absorbance at 205 nm relative to the parent oil. However, both IR and UV do not allow for the determination of individual components of SWSF.

Fluorescence Spectrophotometry

Fluorescence spectrophotometry has been used to monitor very low concentrations of oil in seawater because the sensitivity is greater than that of absorption techniques. Analysis of hydrocarbons in water by UVF was reviewed by the Standing Committee of Analysts (SCA) (1989). In a number of studies, UVF was the technique used to measure the total oil concentration in extracts of SWSF (e.g. Maher 1986; Paine *et al.*, 1992; Sophia and Balasubramanian, 1992). However, as with UV, quantification by UVF also depends on the choice of standard for calibration and is usually measured in equivalents of crude oil or a specific compound such as chrysene (see Table 2.2).

The UVF technique also enables oil to be measured directly in water, thus avoiding the need to make an extract in an organic solvent (e.g. Østgaard and Jensen, 1983b). However, variation in fluorescence properties from mixture to mixture may cause calibration errors. Fluorescence quenching may also occur due to self-absorption in samples of high concentration.

Some qualitative information can be gained by the use of synchronous excitation/emission scanning. The position of the fluorescence band corresponds to the number of fused rings in the compounds causing the fluorescence (e.g. Wakeham, 1977; John and Soutar, 1981). Law (1981) reported that benzene emits most strongly in the 280-290 nm region, naphthalene around 310-320 nm, 3- and 4- ring aromatic compounds between 340 and 380 nm, and compounds with 5 or more rings above 400 nm (Figure 2.4). Busdosh (1981) used synchronous scanning to determine the maximum intensity wavelength in dichloromethane extracts and used them to measure the concentration of oil using calibration curves prepared from whole oil.

However, as only a small proportion of petroleum hydrocarbon compounds fluoresce, UVF is regarded as a semi-quantitative method (Shiu *et al.*, 1990). Theobald (1989) suggested that the combination of high performance liquid chromatography (HPLC) with fluorescence detection allowed for a better characterisation of water extracts and yielded more information about the extract composition than spectroscopic analysis alone.

Gas Chromatography

Gas chromatography (GC) is one of the chromatographic methods most widely used to separate and quantify total and individual hydrocarbons. Lee and Craig (1974) used a known amount of isobutyl acetate as an internal standard to quantify the SWSFs of crude oils. The concentration of total hydrocarbons were calculated from the summation of the individual components.

Lockhart *et al.* (1984) and Murray *et al.* (1984) analysed SWSFs by GC using the headspace technique for the most volatile components and by solvent microextraction for

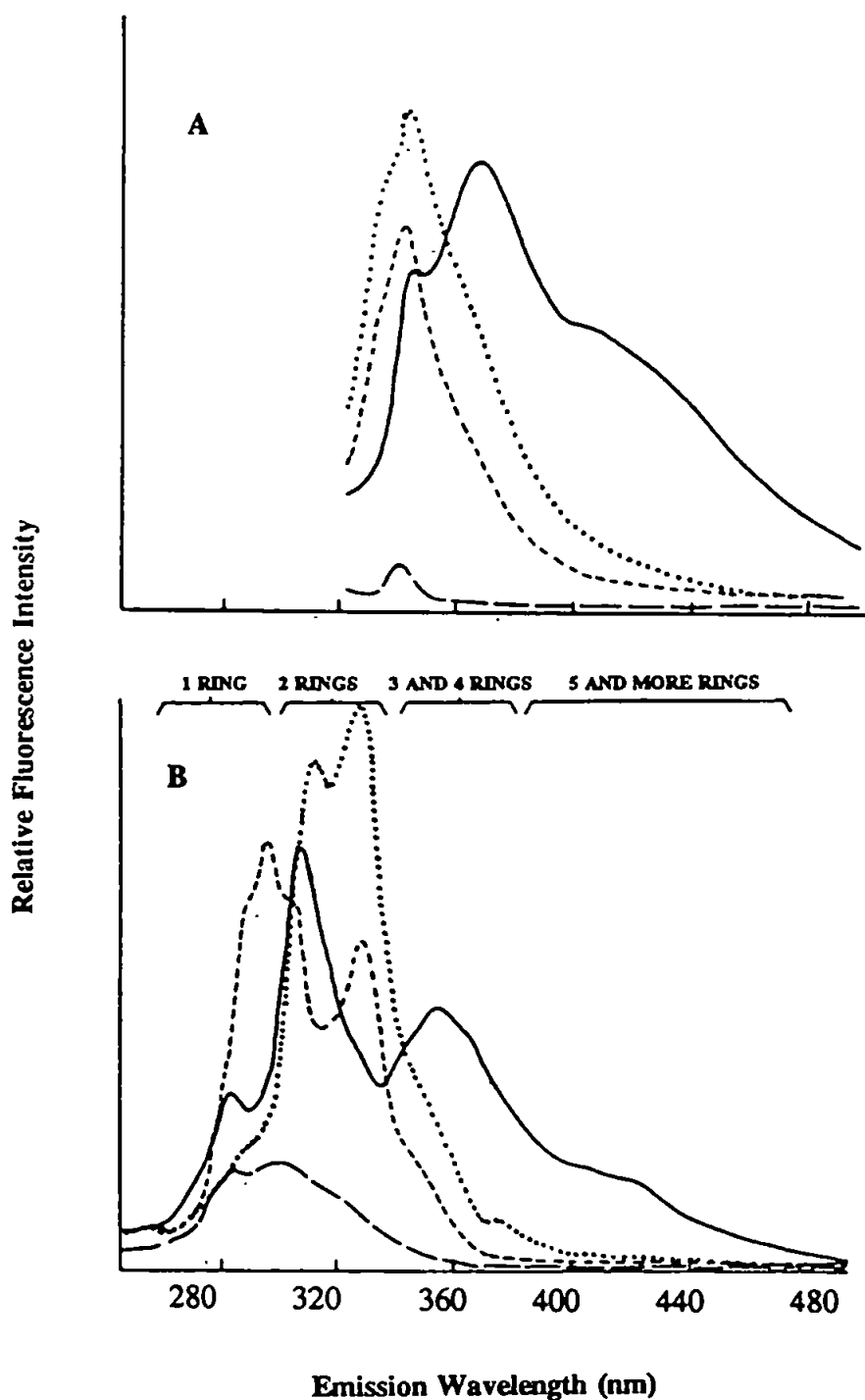


Figure 2.4 Conventional emission (excitation wavelength 310 nm) spectra (A) and synchronous spectra (B) of four column chromatography fractions of Kuwait crude oil: cyclohexane and pentane eluates consist of aliphatic hydrocarbons — — — ; 10% benzene in pentane - - - and 20% benzene in pentane consist of benzenes and naphthalenes; 100% benzene — — — — — consist of aromatics with three or more rings (Wakeham, 1977).

the less volatile materials. The total amount of hydrocarbon present in the SWSF was measured by the summation of quantities associated with 29 identified components quantified with reference to *n*-decylbenzene.

Gravimetry

Gravimetric methods are also used to quantify total dissolved organic residues (e.g. Winters *et al.*, 1976). However, these methods necessitate evaporation to dryness and considerable loss of lighter fractions can occur with a consequent loss of accuracy.

Other Methods

The dissolved organic carbon (DOC) content of water can be a useful indication of the extent of pollution (Mackinnon, 1981). The method commonly used for DOC determination involves three analytical steps: the removal of inorganic carbon from the sample, oxidation of the organic compounds to carbon dioxide; and the quantitative determination of the resulting CO₂.

The oxidation methods can be broadly classed into either wet oxidation where oxidation is performed in the aqueous sample by addition of a chemical oxidant such as persulfate, or combustion methods where the sample is either dried and the resulting residue is oxidized or directly injected into a high-temperature catalytic oxidation system (reviewed by Mackinnon 1981; Wangersky, 1993). Photo-oxidation methods have also been employed for the analysis of DOC. These methods are advantageous for routine analysis and are more easily automated (e.g. Mantoura and Woodward, 1983). However, although this could be a very useful technique, no previous study appears to have used DOC methods for quantifying SWSF extracts of crude oil.

2.2.12 Conclusions of the Literature Review

Careful assessment of the literature suggests that, overall, the slow stirring methods provide a stable saturated mixture of dissolved components provided that the dissolution is carried out in the dark and in a sealed apparatus to avoid losses that occur due to volatilisation or photooxidation. The ratio of oil to seawater influences the concentration of the SWSF; the higher the amount of oil used, the higher the concentration. However there is not a linear relationship between increasing amount of oil added and final concentration (see Anderson *et al.*, 1974). If possible, filtration of samples should be avoided as errors may be introduced by exposure of the sample to the large surface area of the filter (see Law, 1980). It is obviously important that details of preparation methods be reported in order to aid future research.

Since it is apparent that stirring rate and stirring time are important factors, the stirring time required to produce a saturated solution should be verified preferably by a quick analytical method.

2.3 Aims

Although several studies have reported the preparation of SWSF's of crude oil, these studies all have some limitations. Primarily, no standard procedure is available to ensure reliable, reproducible and comparable results. Another limitation is that procedural details are often poorly documented.

The principal objective of the work described in this chapter was therefore to devise an

experimental procedure for the dissolution of Kuwait crude oil in seawater (SWSFs) for use in subsequent photodegradation experiments. This objective was approached in the following way:

1. Development and optimisation of a dissolution procedure which allowed the preparation of a saturated and homogeneous solution of SWSF.
2. Utilisation of the optimised procedure to monitor the dissolution of Kuwait crude oil with time by UVF and DOC analyses.

Confirmation by GC and GCMS with deuterated internal standards is described in detail in the next chapter.

2.4 Experimental

2.4.1 Development of an Optimised Experimental Procedure for the Dissolution of Kuwait Crude Oil in Seawater

As previously discussed, few attempts have been made to develop a standardised procedure which allows the preparation of homogeneous and saturated solutions of seawater soluble fraction (SWSF). The aim of this work was therefore to devise such a procedure. This was eventually achieved by slowly stirring a volume of seawater overlaid by a layer of Kuwait crude oil under carefully controlled conditions. The time required to produce a saturated solution was monitored by ultraviolet-fluorescence spectrophotometry (UVF) and verified by dissolved organic carbon (DOC) analysis. The final procedure was developed over the

course of five experiments. At each experiment, the procedure used to prepare a SWSF was modified, until at the fifth experiment, the procedure was finally optimised and adopted for the measurements of photodegradation rates as will be described in Chapter 5. This section describes the developmental work undertaken to achieve an optimised dissolution procedure, whereas the following section gives details of the quantification of the prepared SWSF solution for the photodegradation experiments.

2.4.1.1 Materials

Unless otherwise mentioned only glass, Teflon or stainless steel equipment was used. All glassware was soaked in chromic acid solution (>48 h), rinsed at least 20 times with distilled water, soaked further in distilled water for *ca.* 2 h and dried (120°C) overnight. Other equipment was soaked in a dilute solution of Decon 90 (3%; >24 h), rinsed thoroughly with hot tap water and distilled water and dried as above. All glassware was rinsed with HPLC grade pentane, hexane or dichloromethane (DCM) immediately before use.

All solvents used in extractions and standard preparations were HPLC grade (Rathburn Ltd., Walkerburn, Peeblesshire, U.K.). Reagents used in sample preparation, including anhydrous sodium sulphate and mercury (II) chloride (HgCl_2), were purchased from the Aldrich Chemical Co. Ltd., Dorset, U.K.

Oxygen-free nitrogen was purchased from Air Products Plc., Chineham, Basingstoke, U.K.

Syringe needles used for addition of the oil and for sampling and 'Suba.Seal' septa, were

purchased from the Aldrich Chemical Co. Ltd., Dorset, U.K. All the remaining apparatus was standard laboratory equipment.

Seawater (salinity 33 ‰; pH 8.4) was collected from the English Channel *ca.* 20 miles south of Plymouth (near the Eddystone lighthouse) in a clean pentane rinsed glass container and filtered through a pre-cleaned Millipore filter (type HA) pore size 0.45 μm .

Kuwait crude oil was obtained from two sources: 1) partially refined crude oil (gas chromatography showed depletion of the alkanes below $n\text{-C}_{12}$) from the Petrochemical Department, Kuwait Institute for Scientific Research (KISR), Kuwait, and 2) fresh (unrefined) crude oil (specific gravity 0.8782, API gravity 29.6° and kinematic viscosity 20.0 centistokes @ 20°C; 10.3 Cst @ 40°C) from the Warren Spring Laboratory, Stevenage, Hertfordshire, U.K., sent in a sealed stainless steel container. Diesel fuel oil was obtained from a filling station (Total) in Plymouth, Devon, U.K.

2.4.1.2 Instrumental Methods

Ultraviolet Fluorescence Spectrophotometry

A Perkin Elmer MPF-3 ultraviolet fluorescence spectrophotometer was used to monitor the dissolution of the oil. UVF analyses were performed by two methods. In the developmental work, the method of Law *et al.* (1988) was used. Measurements were made on the hexane extract at excitation and emission wavelengths of 270 and 330 nm, respectively (which is typical for diesel), using a slit width of 8 nm.

In the experimental work, the UVF measurements were made directly on the water phase

by a method similar to the procedure of Østgaard and Jensen (1983b). The analysis was made by synchronous scanning (200 to 600 nm) with a fixed offset of 25 nm. Excitation and emission slits were adjusted to 5 nm.

The spectrofluorimeter was calibrated with solutions of diesel oil as a reference. Diesel oil (gas oil) was selected as a reference for the quantification of the SWSF by UVF because it is enriched in alkylated benzenes and low molecular weight aromatic hydrocarbons with a similar boiling range to that of the WSF of crude oil (Coleman *et al.*, 1984; Johnson, 1992; Law, 1992). Furthermore, a solution of diesel oil was analysed by synchronous scanning UVF and the excitation-emission spectrum obtained was compared with that of a SWSF analysed under the same conditions. The comparison showed that the composition of diesel oil was similar to the composition of SWSF solution prepared from Kuwait crude oil (Figure 2.5), and was therefore an appropriate reference standard for the samples analysed.

Calibration solutions were prepared from a stock solution ($2000 \mu\text{g mL}^{-1}$) of diesel oil using two methods. In the first method diesel solutions were prepared in hexane. Working solutions between $0\text{--}10 \mu\text{g mL}^{-1}$ (within the linear range of the instrument) were freshly prepared in hexane on the day of the analysis. For the second method, where measurements were made directly on the aqueous phase, the stock solution of diesel was first prepared in ethanol, and volumes between $0\text{--}0.5 \text{ mL}$ were spiked to 100 mL volumes of seawater to make up concentrations between $0\text{--}10 \mu\text{g mL}^{-1}$. To correct for the small additional fluorescence background introduced by ethanol, serial solutions containing the same volume of spiked ethanol in seawater were prepared and analysed together with the samples. Samples found to be outside the linear calibration range were diluted until they

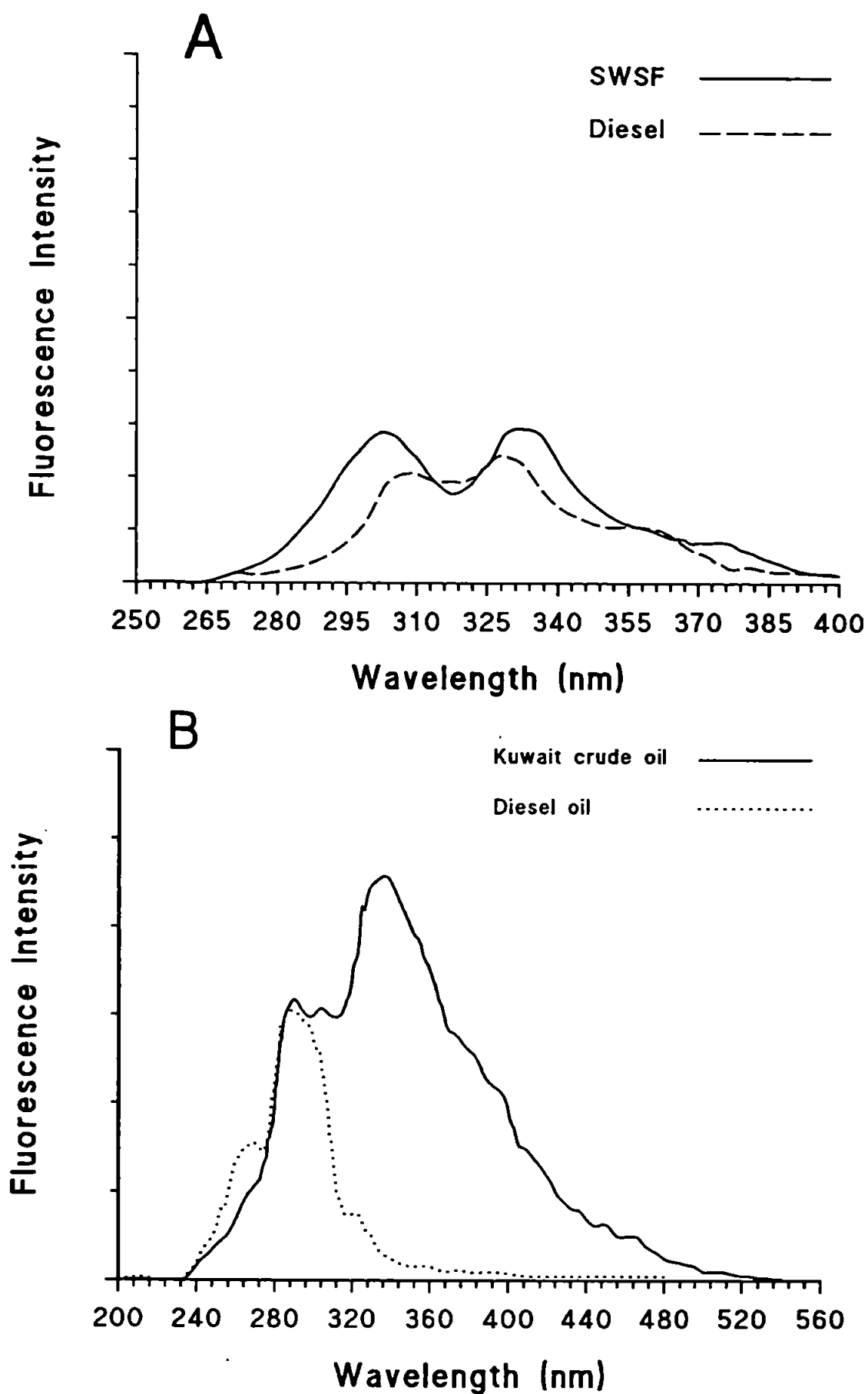


Figure 2.5 Synchronous fluorescence spectra of: (A) diesel oil in seawater and seawater soluble fraction of fresh (unrefined) Kuwait crude oil (25 nm offset scan); (B) diesel oil and Kuwait crude oil in hexane (20 nm offset scan). See text for analysis conditions.

fell within that range. Solvent blanks were examined at the beginning of each sample analysis.

Tap water (temperature range 10-12 °C) was circulated in the cell chamber as the instrument was switched on to minimise the effect of heat produced by the lamp. Fluorescence intensity is very sensitive to changes in temperature (Perkin-Elmer manual). Considerable heat can be generated by the light source, which in turn can effect the measurement of the samples, especially if the samples tend to evaporate with heat.

The objective was to reduce this effect during the analysis by circulating cold tap water around the cell chamber to minimise the effect of the heat produced by the lamp. To investigate the effect of this, measurements of the temperature during operation of the instrument were made. A probe fitted to a data logger (Squirrel 1201 series logger; resolution 0.05 °C; Grant Instruments Ltd, Cambridge, U.K.) was inserted in a cell filled with hexane and the temperature was recorded over a period of 10 hours at 10-minute intervals, both with and without cooling. The results clearly show the effect of cooling on the stability of solvent temperature in the cell (**Figure 2.6**). The temperature increased from 20 to 33 °C in 7 hours without cooling, while with cooling the temperature was almost constant at 14 °C, after 30 minutes from the start of cooling.

The problems of quenching and linearity of the UVF were also investigated to improve the analysis. A blind test was performed using two concentrations (2 and 10 $\mu\text{g mL}^{-1}$) of diesel oil in hexane (both analysed neat and after dilution). Concentration was measured from a calibration curve made with a range of diesel standards within and above the linearity of the UVF. The results obtained showed close agreement with the known concentrations.

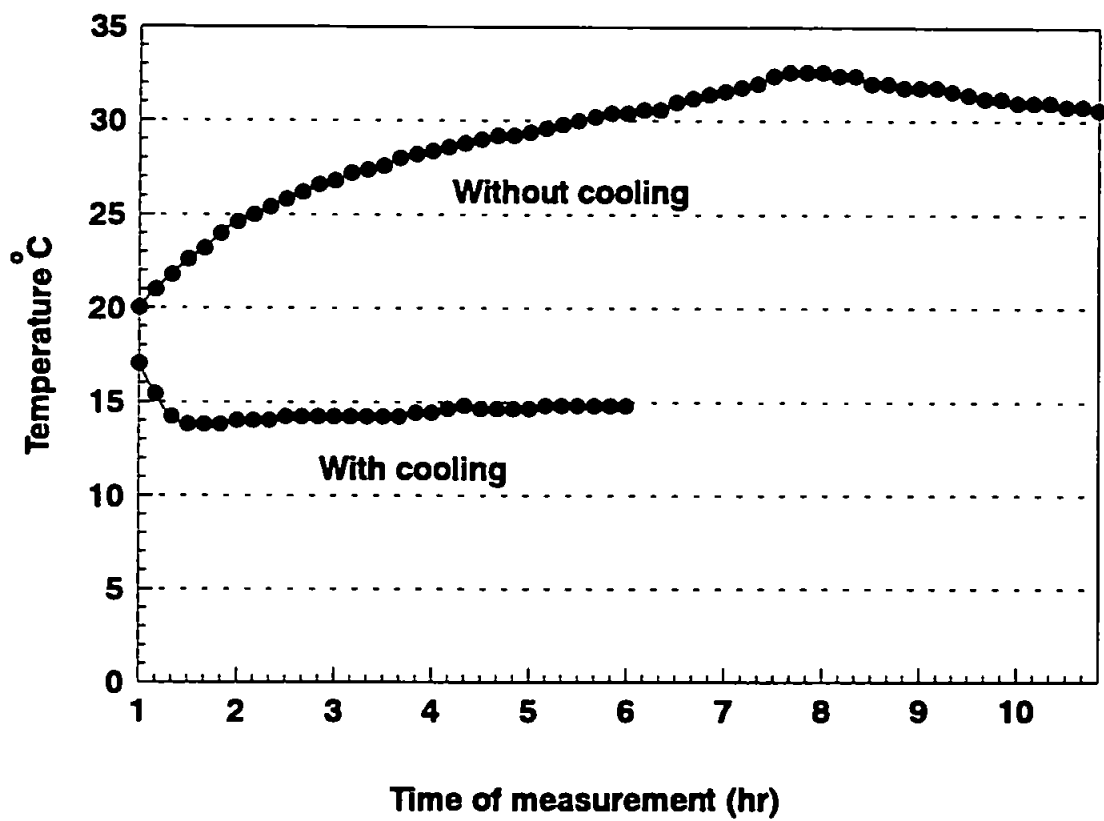


Figure 2.6 The effect of heat from the UVF light source on sample temperature.

Dissolved Organic Carbon Analysis

Dissolved organic carbon (DOC) analyses were performed by two methods. DOC analysis in the developmental part of this research was performed by the method of Miller *et al.* (1993), which was adapted from the method of Sugimura and Suzuki (1988).

A Shimadzu TOC-500 Total Organic Carbon analyzer (Shimadzu Corporation, Koyoto, Japan) was used with the Shimadzu 0.5% Pt/Al₂O₃ catalyst. Analysis was performed by direct injection of a decarbonated liquid sample (80 μ L) onto the catalyst at 680 °C. The reaction produces carbon dioxide gas, which is detected by a non-dispersive infra-red gas analyzer (IRGA). Standards were prepared from a stock solution of 150 mM C-caffeine in Milli-R/Q water in the range between 50 and 300 μ M C. Blanks and the calibrant solutions were analysed before and after sample analysis. A printout on the TOC-500 produces a record of integrated peak area, while graphical output is provided by a non-dedicated chart recorder.

The second method of DOC analysis, performed in the experimental part of this research, was determined by the method of Mantoura and Woodward (1983) using a modified automated UV-photooxidation technique. Prior to DOC analyses, the seawater-derived inorganic carbon (mainly HCO₃⁻) was first removed by acidifying the SWSF samples stored in the vials (5% v/v; 10% H₃PO₄; pH1) and then CO₂ was allowed to diffuse naturally overnight in an operated fume extractor cupboard. Next morning vials containing samples were removed from fume cupboard, capped and taken for analysis. Calibration was prepared by standard addition from 100 mM glucose (as carbon) between 0-750 μ M C into Milli-R/Q water. Samples (5 mL) were analysed in duplicate. Calculation of DOC content for SWSF samples was made from the calibration curve constructed as described

by Peltzer and Brewer (1993).

2.4.1.3 Oil Dissolution Experiment 1.

The oil dissolution procedure started with a very simple arrangement. Filtered sea water (500 mL) was added to a stoppered conical flask (1 L) fitted with a tap about 2 cm from the bottom to aid with sampling (Figure 2.7), and partially refined Kuwait crude oil (5 mL), was placed in a layer on the surface of the seawater with the aid of a syringe connected to a piece of Teflon tube. The resultant oil to water ratio (i.e. 1:100 v/v) was reported to be sufficient to saturate the aqueous phase when preparing a SWSF from crude oil (Lockhart *et al.*, 1984). The mixture was stirred by a magnetic stirring bar which produced an oil vortex of about 1 cm and the apparatus was kept in a fume cupboard at room temperature. Samples were collected at 20 hour intervals. At the time of sampling, stirring was stopped and the solution left to stand for 30 min. After discarding the dead volume occupied in the tap (the volume was verified by measurement), the solution (10 mL) was collected from the tap in a measuring cylinder.

However, after collection of a few samples, the drop in the water level in the flask caused the magnetic stirrer bar to hit the oil layer and disperse the oil in the water. The volume of seawater used (500 mL) could not be increased to avoid this problem because of the shape of the flask (i.e. narrow at the top and wide at the bottom; Figure 2.7) and if a greater volume was used the contact area of the oil layer and the seawater would alter after each sample withdrawal which could affect the dissolution of the oil. Thus an alternative procedure was devised.

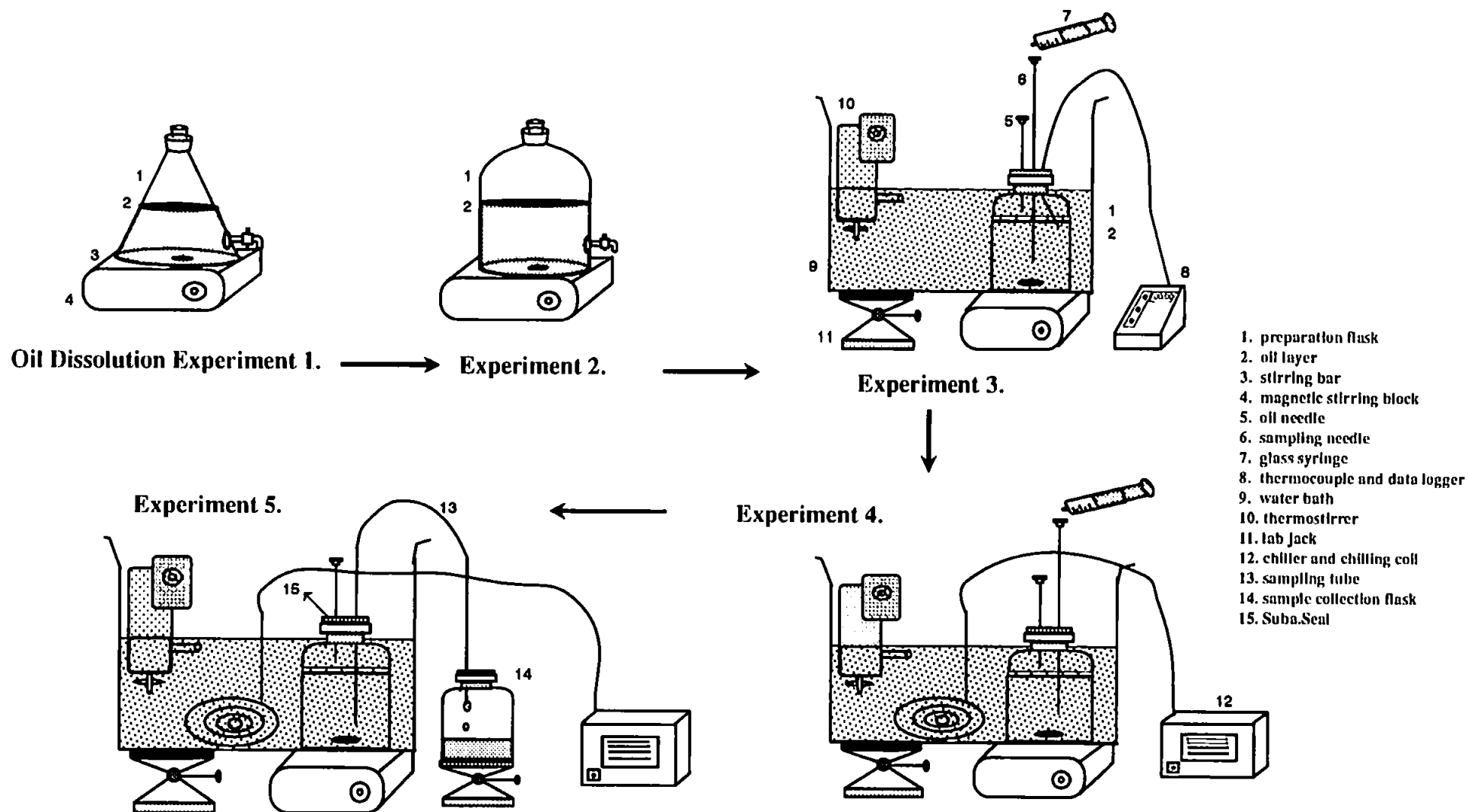


Figure 2.7 Schematic diagrams showing development of the apparatus used in the oil dissolution procedure for the preparation of SWSFs.

2.4.1.4 Oil Dissolution Experiment 2.

The 1 L conical flask was replaced with a 3 L stoppered aspirator bottle fitted with a tap (Figure 2.7). Filtered seawater (1.5 L) was sterilised using HgCl_2 (20 mgL^{-1}), and partially refined Kuwait crude oil (15 mL) was added to the seawater using a glass syringe fitted with a needle. The mixture was stirred with a magnetic stirring bar at low speed. Before sampling, stirring was stopped and the mixture was allowed to stand for 10 minutes. Samples were collected at intervals from 12 hours to 8 days through the aspirator tap and placed in small conical flasks. Solutions of the SWSF (10 mL) were extracted with hexane (10 mL) in a separating flask and dried (10 cm x 1 cm glass columns plugged with defatted cotton wool and filled with pre-extracted anhydrous Na_2SO_4). The dried extracts were collected in 10 mL volumetric flasks. Samples were analysed by UVF as neat and diluted solutions against the calibration solutions as described in Section 2.4.1.2.

Unfortunately, the concentration of the solutions fluctuated erratically over the sampling period (Figure 2.8). The deviation in the concentration could be a result of non-dissolved oil which may have been introduced as a result of variations in the stirring rate as demonstrated previously by, for example, Boylan and Tripp (1971) and Østgaard and Jenson (1983a). However, to confirm that these variations in the concentration were due to dissolution problems and not due to sample work-up, samples of known oil concentration were prepared and analysed.

Three samples of known concentrations of diesel in hexane were added to distilled water ($3, 4$ and $12 \text{ } \mu\text{g mL}^{-1}$), extracted with hexane ($2 \times 5 \text{ mL}$) and collected in small conical flasks into which Na_2SO_4 (4 g) was added. The separating flasks were rinsed with a further

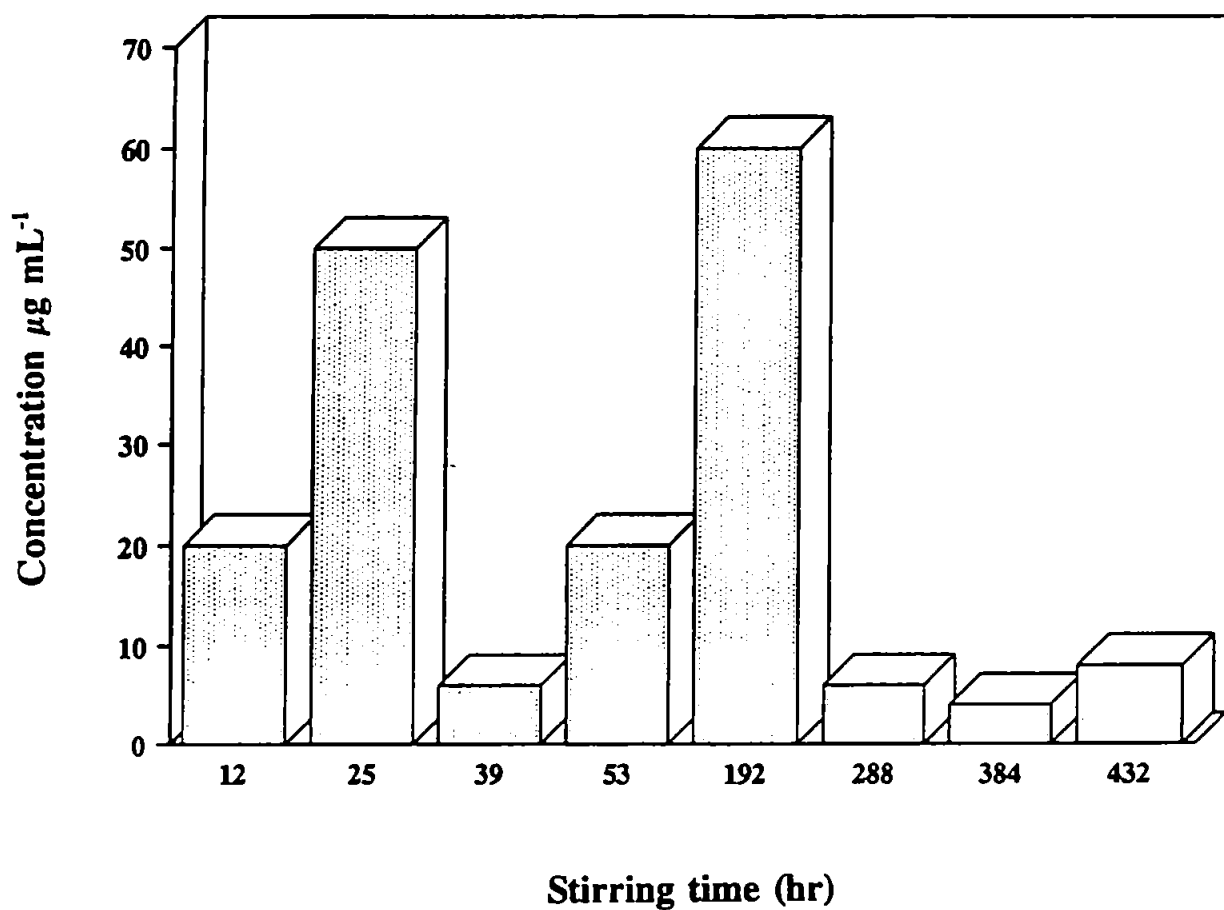


Figure 2.8 Fluctuation of concentration of SWSF of partially refined Kuwait crude oil (diesel equivalent) against time of stirring as obtained from oil dissolution Experiment 2.

5 mL hexane to ensure complete transfer of the sample. The extracts were then made up to 25 mL in volumetric flasks and analysed by UVF. The concentration of the three solutions as read from the diesel in hexane calibration curve were 2, 4, and 10 $\mu\text{g mL}^{-1}$ respectively, indicating reasonable extraction efficiency and analytical measurement and suggesting that the large variations in SWSF (Figure 2.8) were not mainly due to the analytical methods.

It was concluded that variation in the concentration of SWSF shown over the stirring time may have been caused by the sampling technique or stirring rate variation. Therefore further modifications to the sampling technique were made and particular attention was given to the stirring rate. In addition to this, arrangements were made to carry out the dissolution under a constant temperature and in darkness.

2.4.1.5 Oil Dissolution Experiment 3.

The aspirator flask used in experiment 2 was replaced by a reagent flask (1L), sealed with a 'Suba.Seal' septum, through which 2 syringe needles were inserted. One needle (2", 18-gauge stainless steel; with female luer hub and deflecting tip) was used for the addition of the oil and the second needle (12", 22-gauge stainless steel, with female luer hub and deflecting tip) for the withdrawal of SWSF solutions. The flask was placed in a plastic tank filled with tap water which circulated around the flask with the aid of a stirrer. The water bath temperature was read from a thermometer, and the temperature of the solution inside the preparation flask was recorded with a data logger as before (Figure 2.7).

Filtered seawater (900 mL) was transferred into the flask and sterilised using HgCl_2 (20

mgL⁻¹). The 'Suba.Seal' was prepared by inserting the two syringe needles and the temperature probe and before fitting it to the neck of the flask a magnetic stirrer (2 cm) was added and the flask headspace was flushed with a stream of purified nitrogen gas to eliminate air. The flask was sealed with the 'Suba.Seal' septum, ensuring the needle used to add the oil was kept just above the water surface and that the sampling needle was deep in the water and away from the oil layer. The flask (which was secured with a lead 'doughnut') was placed in the water tank and the tank was placed on a magnetic stirrer block on one side and supported by a jack from the other side (**Figure 2.7**). Kuwait crude oil (9 mL, partially refined) was taken up using a glass syringe and layered carefully drop by drop on top of the seawater surface. Finally, the whole apparatus was covered with a black plastic sheet to avoid photodegradation by laboratory lights. The water was stirred slowly at a constant speed of 150 rpm (measured by Griffin Xenon Stroboscope).

Before withdrawing any samples the temperature of the solution was examined. It was found that the heat generated from the stirrer had raised the water temperature in the tank 5 °C within 5 hours, and it continued to rise with time, thus affecting the temperature of the solution. As the process of oil partitioning into water column is sensitive to temperature (Gearing and Gearing, 1982) the rise in the temperature was deemed unacceptable and a further modification was made.

2.4.1.6 Oil Dissolution Experiment 4.

Problems encountered with the unstable water bath temperature were overcome with a thermostated water bath fitted with a cooling coil and heater-stirrer unit (**Figure 2.7**). A temperature of $25 \pm 1^\circ\text{C}$ was maintained using this arrangement (i.e. average summer water

temperature of the Arabian Gulf surface sea-water; al-Abdul-Razzak, 1984).

The preparation of the SWSF solution was as described in Section 2.4.1.5 using the same oil. Sampling was carried out in duplicate by slowly withdrawing SWSF solutions (10 mL) with a glass syringe and sampling needle without interrupting the stirring. Sampling times were from 2 hours to 151 hours.

Samples were extracted with hexane (2 x 5 mL) and passed through a micro-column (Pasteur pipette plugged with cotton wool and filled with anhydrous Na_2SO_4). The column was washed with a further 5 mL hexane and the dried extract was made up to 20 mL in a volumetric flask. Samples were analysed by UVF as described in Section 2.4.1.2.

The results showed that dissolution increased slowly but steadily as a consequence of the modifications introduced following experiment 2 (Figure 2.9). A good agreement was demonstrated between the duplicates analysed and the maximum concentration reached was about $1 \mu\text{g mL}^{-1}$ (as diesel equivalent) at 100 hours (Table 2.3). The concentration of the SWSF was stable after 4 days of slow stirring. However, this concentration was lower than expected from the literature for Kuwait oil and seawater stirred constantly for 6 days. Concentrations cited in the literature vary between 0.5 to $12.7 \mu\text{g mL}^{-1}$ after stirring seawater for 24 hours with Kuwait crude (calibrated vs. Kuwait crude, e.g. Boylan and Tripp, 1971; Anderson *et al.*, 1974; Blackman and Law, 1980; Sophia and Balasubramanian, 1992). To allow direct comparison with these values the present UVF measurements were calibrated with both Kuwait crude oil (partially refined) and with diesel solutions in hexane between $0\text{--}1 \mu\text{g mL}^{-1}$ (Figure 2.10). A correction factor was calculated from the two calibration curves (see Table 2.3) and applied to all results

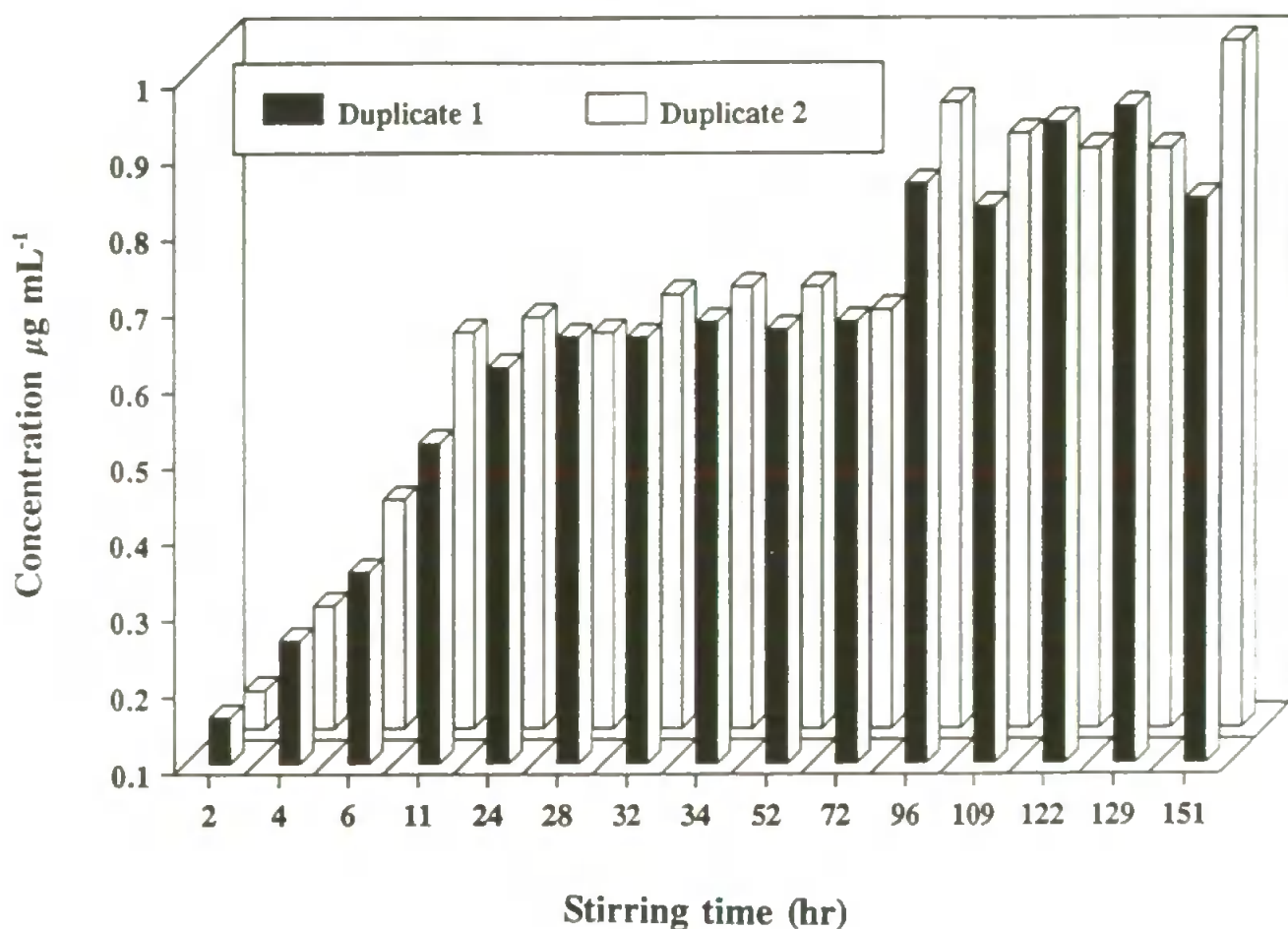


Figure 2.9 Steady increase in concentration of SWSF of partially refined Kuwait crude oil (diesel equivalent) with time of stirring as obtained from oil dissolution Experiment 4.

Table 2.3 Concentration of SWSF of partially refined Kuwait crude oil with respect to stirring time as obtained from oil dissolution Experiment 4.

Stirring Time (hr)	Concentration $\mu\text{g mL}^{-1}$ (Diesel equivalent)			Concentration $\mu\text{g mL}^{-1}$ ^a (Kuwait crude equivalent)		
	Duplicates		Average	Duplicates		Average
2	0.16	0.15	0.16	1.2	1.1	1.2
4	0.26	0.26	0.26	1.9	1.9	1.9
6	0.35	0.40	0.37	2.6	3.0	2.8
11	0.52	0.62	0.57	3.5	4.6	4.0
24	0.62	0.64	0.63	4.6	4.7	4.7
28	0.66	0.62	0.64	4.9	4.6	4.8
32	0.66	0.67	0.67	4.9	5.0	5.0
34	0.68	0.68	0.68	5.0	5.0	5.0
52	0.67	0.68	0.68	5.0	5.0	5.0
72	0.68	0.65	0.67	5.0	4.6	4.8
96	0.86	0.92	0.89	6.4	6.7	6.6
109	0.83	0.88	0.89	6.0	6.5	6.3
122	0.94	0.86	0.90	7.0	6.4	6.7
129	0.96	0.86	0.91	7.1	6.4	6.8
151	0.84	1.00	0.92	6.2	7.4	6.8

^a Concentrations were calculated according to the following formula:

$$H_c = H_d * \frac{D}{C}$$

H_c = Hydrocarbons based on crude oil calibration

H_d = Hydrocarbons based on diesel oil calibration

D = Slope of diesel calibration curve (see Figure 2.10)

C = Slope of crude oil calibration curve (see Figure 2.10)

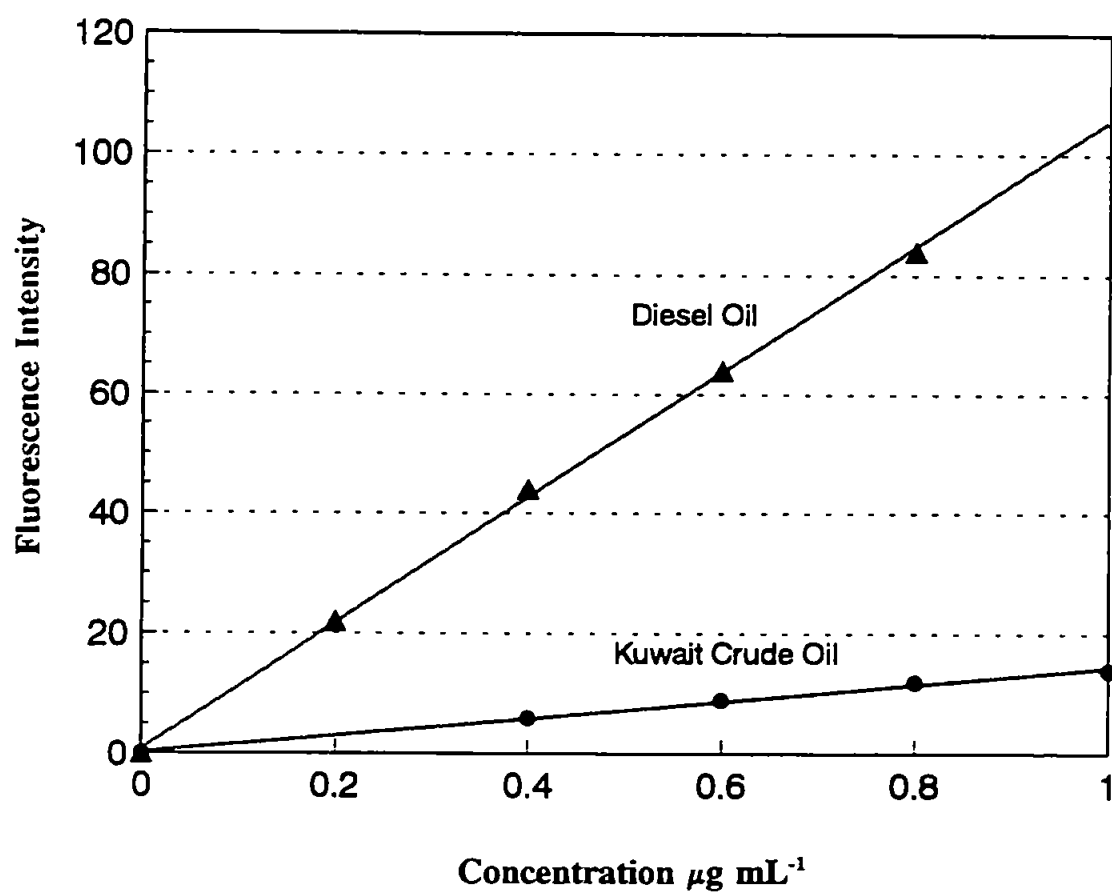


Figure 2.10 UVF calibration curves of diesel oil and partially refined Kuwait crude oil in hexane (see text for analysis conditions).

obtained using the diesel calibration curve.

The concentration of SWSF solution calculated from the calibration curve of Kuwait crude oil was found to be higher by a factor of 7.4 compared to results based on the diesel calibration curve. This difference reflects the very different composition of crude oil and the SWSF of Kuwait crude oil as will be discussed in more detail in the next chapter. SWSF has a composition much closer to that of diesel as discussed earlier (Section 2.4.1.2) and hence it is felt that SWSF concentrations are more appropriately expressed as diesel equivalents.

DOC Analysis

Since the concentration of SWSF hydrocarbons as measured by UVF were lower than expected, they were verified by a second analytical method.

Three samples of SWSF were collected in duplicate from the solutions prepared in Experiment 4 at stirring times of 11, 12 and 13 days. The DOC concentrations of the first set were determined and the second were analysed by UVF according to the procedure described in Section 2.4.1.2. The results of the two analyses were compared.

DOC was determined by two procedures; with acidification and immediate removal of CO₂ by bubbling N₂ through the sample, followed by direct injection of the decarbonated samples into the Shimadzu TOC 500; and with acidification, but without bubbling N₂ through the sample, thus allowing the CO₂ to be evolved naturally. DOC was measured over a period of time until a constant value was obtained. The second method was employed to establish whether bubbling the sample with N₂ removed any volatile components of the SWSF.

Comparison of SWSF Concentrations Determined by DOC and UVF in Experiment 4.

The concentration (as diesel equivalent) obtained by UVF of the three samples (corrected for blanks) did not exceed $1 \mu\text{g mL}^{-1}$ ($0.84\text{--}1 \mu\text{g mL}^{-1}$) as shown in Table 2.4 and no further increase in SWSF concentration was observed beyond that obtained previously after stirring for 6 days. When the concentrations were re-calculated on the basis of Kuwait crude oil calibration curve, they were between 6.2 and $7.7 \mu\text{g mL}^{-1}$.

Results of the DOC analysis after correction for blanks, are also given in Table 2.4. Results obtained from the two acidification procedures are quite similar. The concentration determined by DOC analysis was between 1.8 and 3.2 for day 11 to day 13, expressed in $\mu\text{g C mL}^{-1}$ seawater. This is higher than the concentrations obtained by UVF and may be due to the differences between the two methods (e.g. UVF dependency on oil composition and calibrant; potential losses of volatiles and incomplete removal of CO_2 might occur with DOC analysis; Standing Committee of Analysts, 1989; Wangersky, 1993). However, as crude oil is only 80% carbon, the results need to be recalculated to obtain $\mu\text{g oil mL}^{-1}$. The recalculation showed that the concentration was between $2.3\text{--}4.0 \mu\text{g oil mL}^{-1}$.

In conclusion, the concentration as determined by UVF and DOC ranged between $0.84\text{--}7.7 \mu\text{g mL}^{-1}$ seawater and would provide sufficient starting material for the photodegradation experiments.

Further Modifications of the Dissolution Apparatus

The fourth apparatus, when utilised for preparing SWSF solution for analysis, exhibited new sampling problems associated with the withdrawal of a larger volume of solution (i.e. 50 mL) which were not shown with the withdrawal of the small volumes (i.e. 10 mL)

Table 2.4 Concentration of SWSF of partially refined Kuwait crude oil as measured by DOC and UVF analyses in oil dissolution Experiment 4.

DOC							UVF	
Stirring Time (Days)	Without N ₂ Bubbling ($\mu\text{g C mL}^{-1}$) Time elapsed after acidification				With N ₂ Bubbling		Diesel Equivalent	Kuwait Crude Equivalent
	0 hr	7 hr	10 hr	20 hr	$\mu\text{g C mL}^{-1}$	$\mu\text{g Oil mL}^{-1} *$	$\mu\text{g mL}^{-1}$	$\mu\text{g mL}^{-1}$
11	11.3	2.8	2.1	2.2	1.8	2.3	1.04	7.7
12	9.7	3.4	2.6	2.9	2.3	2.9	0.84	6.2
13	9.7	4.2	3.7	3.9	3.2	4.0	0.92	7.0

* $\text{Carbon}_{(\text{Oil})} = \text{Carbon}_{(\text{DOC})} * 100/80$

associated with the developmental work. Withdrawal of 50 mL of solution using a 50 mL glass syringe and the already inserted needle, resulted in a slightly reduced pressure inside the preparation flask and following release of the syringe from the needle allowed air to flow into the flask, causing agitation of the oil/water interface. The agitation could result in a different concentration level of SWSF after withdrawing each sample. Therefore, a fifth SWSF preparation system was employed to overcome this problem.

2.4.1.7 Oil Dissolution Experiment 5.

Figure 2.7 shows the modified arrangements for sampling the SWSF solution. A stainless steel "U-tube" (80 cm; 0.1 cm o.d.) replaced the withdrawal needle previously used. One end of this tube was inserted in the preparation flask before addition of the oil and the other end was inserted into a collection flask. Both flasks were sealed with 'Suba.Seals' to ensure that no solute was lost during preparation and sampling.

To begin collection of the SWSF solution nitrogen was allowed to flow gently into the preparation flask through the oil addition needle, which was left in position after adding the oil. As the pressure of nitrogen built up, the SWSF solution flowed into the "U-tube" and collected in the flask without disturbing the oil/water interface. When collection was completed, the flow of nitrogen was stopped and the collection flask was raised with the aid of a jack to prevent more of the sample seeping through.

The SWSF stock solution was then stored in a refrigerator at 4 °C and used within 3 days. However, with the amount of biocide added for sterilisation, the solution should be stable for at least a week (see Literathy *et al.*, 1989). The SWSF solution could also be collected as subsamples in smaller volumes as required, simply by using different sizes of collection

flasks.

This optimised experimental procedure for the dissolution of oil was used thereafter to prepare SWSF of Kuwait crude oil for the photodegradation experiments as detailed in the next section.

2.4.2 Preparation of SWSF Using the Optimised Procedure

The final design of the apparatus described above and used in the following experiment is shown in **Figure 2.7**. The SWSF was prepared from unrefined Kuwait crude oil and filtered seawater. Seawater (900 mL) was poured into a 1 L glass reagent flask (20 cm total height; 9.13 cm, o.d.) and sterilised using 20 mgL⁻¹ HgCl₂ (see Literathy *et al.*, 1989). Fifty mL of the sterilised seawater was separated for blank analysis. A Teflon-coated magnetic stir bar (2 cm x 0.5 cm) was added and the flask head space was flushed with pure nitrogen to eliminate any air present before the flask was sealed tightly with a 'Suba.Seal' septum. A syringe needle (2"; 18-gauge stainless steel; with female luer hub and deflecting tip) was inserted into the 'Suba.Seal' septum close to the surface of the seawater to allow the addition of oil. A stainless steel "U-tube" (80 cm long; 0.1 cm o.d.) for the collection of the SWSF was also inserted through the Suba.Seal into the seawater, well below the oil layer. The other end of the tube was inserted into another Suba.Seal connected to a collection flask of suitable size. The collection flask was placed on a jack next to the water bath.

Before adding the oil, the temperature of the seawater in the flask was brought to 25 ± 1 °C by placing the whole flask in a thermostated water bath. The water bath containing the

preparation flask was placed on a magnetic stirring block positioned under the flask and the other end of the water bath was supported by a jack. The crude oil (9 mL) was added drop by drop close to the seawater surface to form a thin layer (measured surface area 65.4 cm²; calculated thickness 1.4 mm). Slow stirring at a constant speed of 150 rpm ensured that mixing took place without the formation of an oil-in-water emulsion. The whole apparatus was covered with a black plastic sheet to avoid photodegradation by laboratory lights.

Sampling through the "U-tube" was carried out without interrupting stirring by applying a gentle stream of nitrogen to the top of the oil/seawater surface through the oil addition needle which was left in place after adding the oil. When each SWSF collection was complete the flow of nitrogen was stopped and the collection flask was raised with the aid of the jack to prevent more sample from seeping through. Each SWSF sample was split into duplicates and stored in large capped vials. One SWSF duplicate was examined by UVF analysis and the other by DOC analysis. A summary of the SWSF preparation conditions is given in Table 2.5.

2.4.2.1 Determination of the Concentration of Oil in SWSF

The dissolution of Kuwait crude oil with respect to stirring time was determined by UVF and DOC analysis. UVF measurements of duplicate SWSF samples were made directly in the water phase as described in Section 2.4.1.2. The samples were analysed as neat extracts and also after dilution to exclude any quenching effects. Seawater blanks were also examined and the small additional fluorescence background introduced by ethanol was corrected for in the treatment of the data as described earlier. DOC was determined using

Table 2.5 Summary of preparation conditions of SWSF of a Kuwait crude oil used in the optimised dissolution procedure.

Parameter	Measurement
Flask dimensions (length, o.d.)	20 cm, 9.13 cm
Volume of seawater	900 mL
Height of seawater column	14 cm
Volume of crude oil	9 mL
Weight of crude oil	7.9 g
Oil slick above seawater	65.4 cm ² ; 1.4 mm thick
Stirring rate	150 rpm
Size of magnetic stirring bar	2.5 cm x 0.5 cm
Water bath temperature	25 ± 1 °C
Sampling tube (length, o.d.)	80 cm, 0.1 cm o.d
Oil addition needle (length, size)	2", 18-gauge

an automated UV-photooxidation analyzer. The procedure of analysis has been described in Section 2.4.1.2.

2.5 Results and Discussion

2.5.1 UVF

Many studies have used UVF spectroscopy to monitor oil in water concentrations. Indeed, UVF is used as a standard method for oil in water analysis (Standing Committee of Analysts (SCA), 1989). The method relies on fluorescence of the more water soluble aromatic components of oil. However, whilst sensitive, it is very dependent on oil composition and suitable calibrants must be used (SCA, 1989).

Synchronous-fluorescence analysis is a particularly advantageous qualitative approach in the determination of petroleum hydrocarbons in water because it provides information about the aromatic composition and the dominant soluble class of compounds, according to ring number (Wakeham, 1977). The fluorescence spectra obtained from the SWSF produced by slow stirring of a layer of Kuwait crude on seawater for up to 10 days and from the diesel standard are presented in Figure 2.11. Comparison of spectra for SWSF and diesel oil showed a similarity between the emission wavelength characteristics in that both showed emission in the 265-385 nm region indicating the presence of from one to four fused aromatic rings (Law, 1981). Maximum emission in both were exhibited in the 296-310 nm region and in the 320-330 nm region which indicated that diesel contained aromatic hydrocarbons similar to the content of SWSF. The emissions in these two particular regions are indicative of the presence of benzene and naphthalenes, respectively

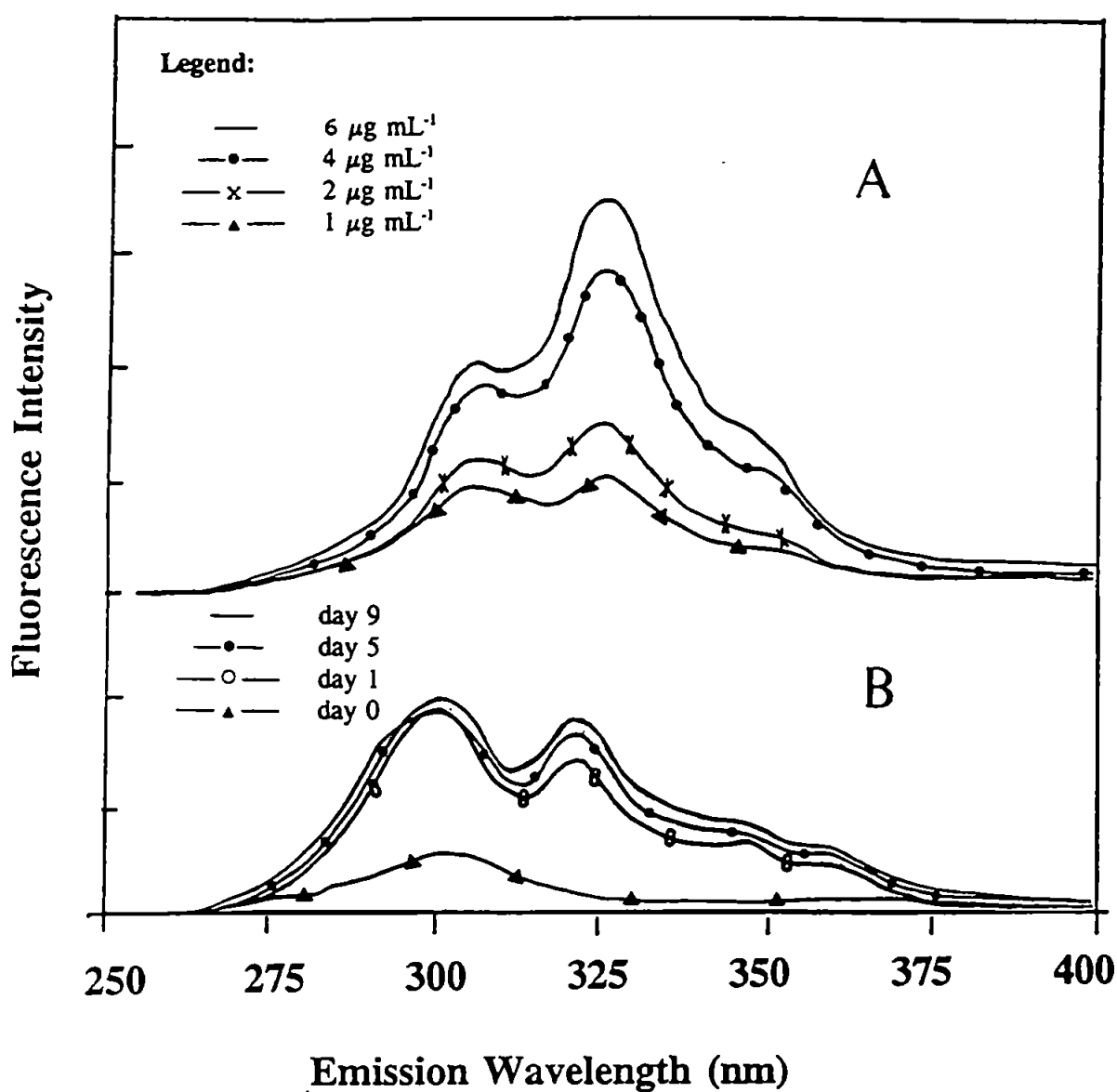


Figure 2.11 Synchronous fluorescence spectra (25 nm offset scan) of: (A) diesel oil in seawater and (B) seawater soluble fraction of unrefined Kuwait crude oil prepared using the optimised dissolution procedure.

(Wakeham, 1977). Similar emissions were reported by Østgaard and Jenson (1983a) for a slowly stirred seawater solution of Ekofisk crude oil. Therefore, the results were expressed as diesel equivalent and were calculated from the synchronous spectra based on the UVF response (measured in arbitrary units) for the wavelength which gave maximum fluorescence in the diesel solutions (i.e. 325 nm, **Figure 2.11**). The concentration of oil in the SWSF increased with stirring time as shown in **Figure 2.12** and the duplicate was in good agreement. The greatest increase occurred in the first 2 days of continuous slow stirring (0.1 to 2.3 $\mu\text{g mL}^{-1}$ as diesel equivalent). A slower, more gradual increase occurred thereafter, reaching a maximum of 2.6 $\mu\text{g mL}^{-1}$ seawater at day 9 (**Table 2.6**). The sensitivity of direct fluorometry should allow concentrations as low as 0.6 ng mL^{-1} to be detected (Østgaard and Jenson, 1983b) and therefore allows for small increments in oil dissolution to be quantified satisfactorily. The decrease to 2 $\mu\text{g mL}^{-1}$ at day 10 was unexpected and may be due to microbial activity despite the addition of HgCl_2 biocide.

The higher concentrations obtained from the unrefined Kuwait crude oil as compared to concentrations obtained previously from the partially refined oil (maximum 1 $\mu\text{g mL}^{-1}$; see Section 2.4.1.6), clearly suggest that low boiling point hydrocarbons contribute substantially to the total hydrocarbon composition of the SWSF. This is in agreement with the finding of Soto *et al.* (1974) and Mackay and Shiu (1976) using weathered crude oil. The environmental significance of these findings are of potential importance to toxicity studies since it appears that the key toxic components are contained within the volatile fraction of crude oil (Kauss *et al.*, 1973).

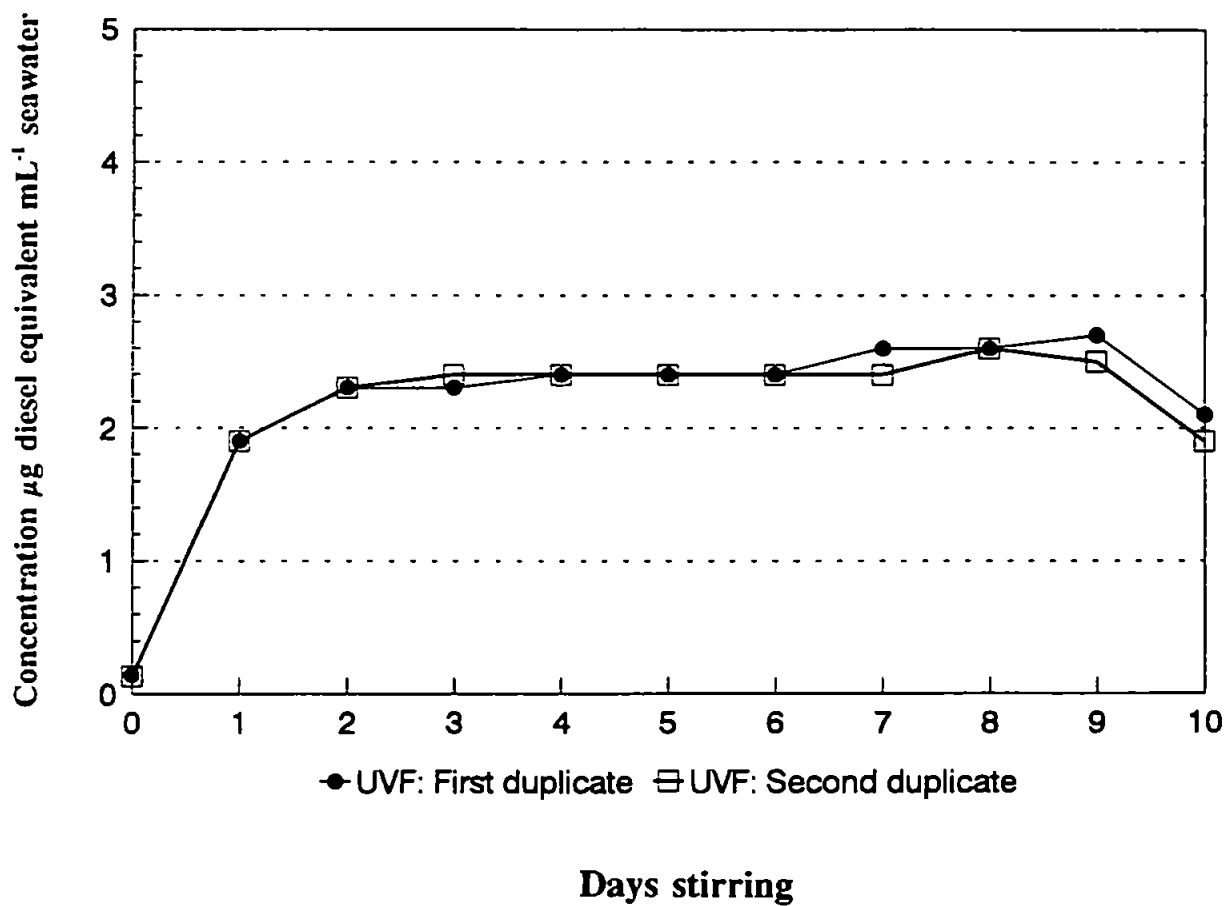


Figure 2.12 Dissolution of fresh (unrefined) Kuwait crude oil with respect to stirring time obtained using the optimised preparation procedure as measured by UVF.

Table 2.6 Comparison of concentrations of SWSF of unrefined Kuwait crude oil with respect to stirring time as measured by UVF and DOC analysis.

Stirring Time (days)	UVF $\mu\text{g mL}^{-1}$ seawater (Diesel equivalent)			DOC $\mu\text{g C mL}^{-1}$ seawater	
	Duplicates		Average	Duplicates	
0	0.14	0.13	0.1	0.1	n.d
1	1.9	1.9	1.9	1.0	0.8
2	2.3	2.3	2.3	1.9	1.1
3	2.3	2.4	2.4	2.1	1.5
4	2.4	2.4	2.4	2.4	1.5
5	2.4	2.4	2.4	3.6	3.2
6	2.4	2.4	2.4	2.7	2.3
7	2.6	2.4	2.5	3.3	2.3
8	2.6	2.6	2.6	2.2	1.8
9	2.7	2.5	2.6	4.3	3.4
10	2.1	1.9	2.0	3.0	2.9

n.d not determined

2.5.2 DOC

The results of the DOC analysis of the oil in SWSFs are shown in **Figure 2.13**. As with UVF determination, the major increase in oil concentration was between day 0 and day 2 ($0.1 - 2.3 \mu\text{g C mL}^{-1}$ seawater) (**Table 2.6**). The maximum concentration of $4.3 \mu\text{g C mL}^{-1}$ seawater in the first duplicate and $3.4 \mu\text{g C mL}^{-1}$ seawater in the second duplicate, was obtained for the day 9 samples. Duplicates gave somewhat different results to each other, with the first measurement always higher than the second. However, difficulties associated with DOC procedures are well known (Suzuki, 1993) and there is a general agreement between the DOC analyses and the UVF measurements.

The results obtained in this study are well within the range of concentrations reported previously of $0.5 - 12.7 \mu\text{g mL}^{-1}$ obtained using an oil to seawater ratio of 1:9 - 1:60 (Boylan and Tripp, 1971; Anderson *et al.*, 1974; Blackman and Law, 1980; Sophia and Balasubramanian, 1992).

2.5.3 UVF Versus DOC

Despite the disadvantages with any one method of analysis of oil in water (Burns, 1993), very few studies have used more than one analytical method to monitor oil dissolution. UVF and DOC methods can be considered as complementary since UVF is sensitive but is dependent on oil composition, especially the content of polyaromatic hydrocarbons. DOC is relatively insensitive and somewhat irreproducible because of the potential loss of volatiles during CO_2 diffusion from acidified seawater (benzene and toluene make up 60% of SWSF, see Chapter 3). In addition, DOC is not specific to the measurement of

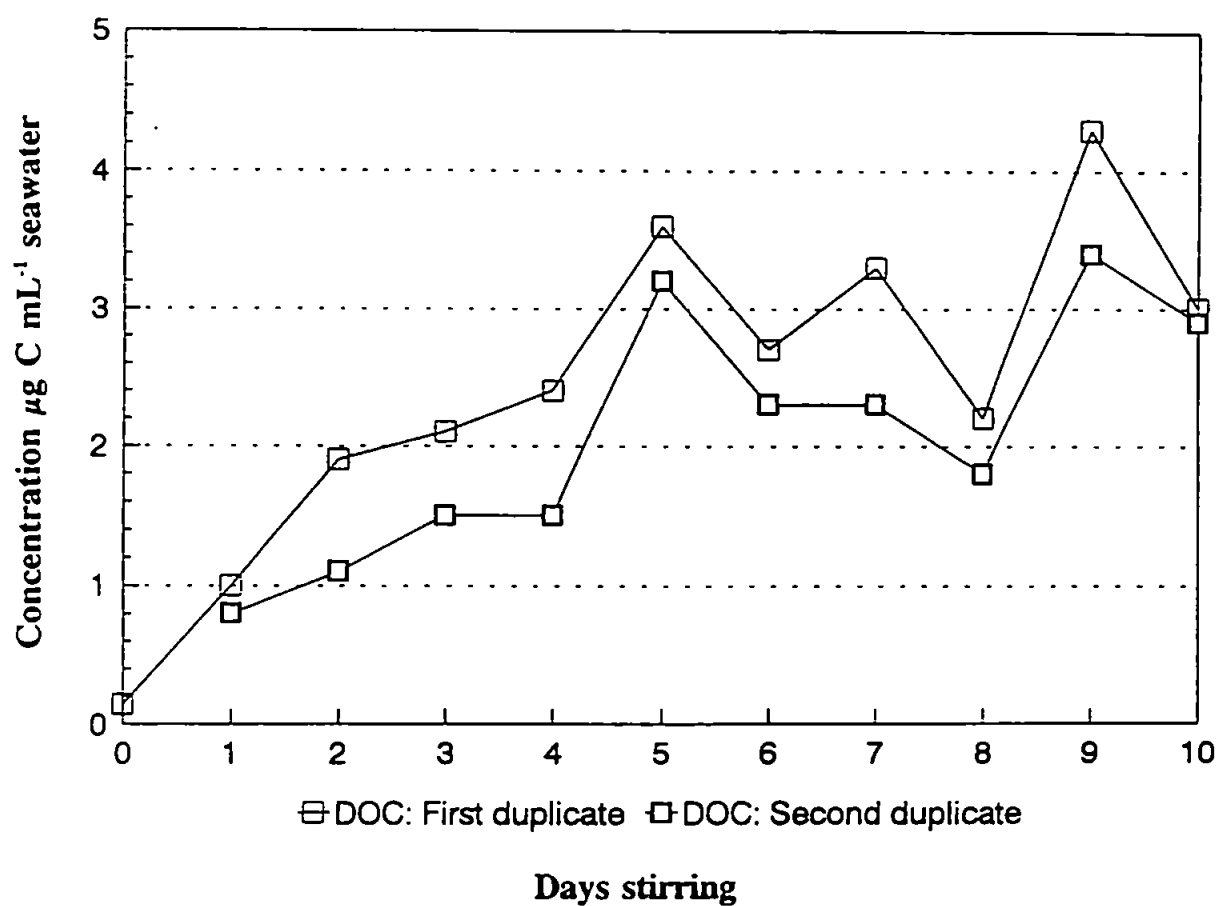


Figure 2.13 Dissolution of fresh (unrefined) Kuwait crude oil with respect to stirring time obtained using the optimised preparation procedure as measured by DOC.

fluorescent aromatics. Therefore the two methods would not be expected to give identical results but should follow a similar trend. These aspects were reflected in the results obtained in this study, where DOC values fluctuated between $2\ \mu\text{g mL}^{-1}$ and $4.3\ \mu\text{g mL}^{-1}$ seawater (as Carbon) whilst UVF results remained between $2\text{--}3\ \mu\text{g mL}^{-1}$ seawater (as diesel equivalent). Although both UVF and DOC methods are less specific and considerably less accurate than GC-MS (as will be seen from the comparison between these three methods in the next chapter), they have the advantage that they are much faster and less costly.

Overall, the results obtained from UVF and DOC show the same trends and provide an adequate monitor of the kinetics of oil dissolution. Dissolution equilibrium is achieved after 5 days of gentle stirring at $25\pm 1\ ^\circ\text{C}$. Accurate analyses were made by the more specific GC-MS method on 5 day equilibrated samples (see Chapter 3).

2.5.4 Comparison With Other Studies

The preparation of a seawater soluble fraction (SWSF) of oil in water is not a simple process and a variety of methods have been adopted by previous researchers (e.g. Lockhart *et al.*, 1984; Shiu *et al.*, 1990; Paine *et al.*, 1992). Crude oil components have an appreciable but limited solubility in seawater and solubility is affected by numerous factors including the oil to water ratio, the composition of the oil, water temperature and salinity as reviewed in Section 2.2. A particular problem for the preparation of reproducible SWSFs is the formation of an oil-in-water emulsion which is often influenced, to a large extent, by stirring rate (e.g. Boylan and Tripp, 1971; Soto *et al.*, 1974). Cited values from experimental studies using Kuwait crude oil, range from 0.5 to $12.7\ \mu\text{g mL}^{-1}$ oil in water using slow stirring methods for up to 24 hr (Boylan and Tripp, 1971; Anderson *et al.*,

1974; Blackman and Law, 1980; Sophia and Balasubramanian, 1992).

The results obtained from this work for the determination of the content of SWSF solution are compared in Table 2.7 with other laboratory studies using Kuwait crude oil and slow stirring techniques. For example, Blackman and Law (1980) used a slow stirring rate (24 hr) with an oil to water ratio of 1:9 at 20°C, which produced 650-1000 $\mu\text{g L}^{-1}$ of SWSF (Kuwait crude oil equivalents) when measured by UVF. The same ratio and temperature was used by Sophia and Balasubramanian (1992), who reported 1270 $\mu\text{g L}^{-1}$ by UVF (Kuwait crude equivalent) after 20 h of slow stirring. The result obtained from this work was 1900 $\mu\text{g L}^{-1}$ of SWSF (as diesel equivalent). This concentration is considerably higher than the above two results, as measured by a similar technique (UVF) but at 25 °C and at an oil to water ratio 11 times lower (1:9 versus 1:100) using about the same stirring time (24 hr). Although the concentration of SWSFs may be indicative of the relative amount of oil initially added (e.g. Busdosh, 1981), the results of this study strongly suggest that other factors such as the rate of stirring, temperature, and volatile losses (benzenes compose a major fraction of SWSF; Pearson *et al.*, 1980; Murray *et al.*, 1984) will influence the final concentration of the solution (see Section 2.2 for a review on these factors).

Equally important in the process of oil dissolution is the method of quantification. The influence of this has already been demonstrated by the results obtained for the SWSF by two independent methods (i.e. UVF and DOC). To further illustrate this point, comparison is made with studies carried out using other methods of quantification. Boylan and Tripp (1971) measured the total amount of oil in water prepared from an oil to water ratio of 1:60 by GC. The total pentane extract (volatiles below 1,3-dimethylbenzene were not recovered) was found to be 1453 $\mu\text{g L}^{-1}$, after 12 h of slow stirring. Furthermore, the

Table 2.7 Comparison of concentration determined in this study with studies reporting the preparation of seawater soluble fraction of Kuwait crude oil.

Year	Author	Oil to Water Ratio	Method of Preparation	Stirring Time (hr)	Water Temperature °C	Method of Quantification	Concentration $\mu\text{g L}^{-1}$
1971	Boylan & Tripp	1:60	Stirring : slow, 25 % oil vortex Flask : stoppered Standing time : not reported	12	23	GC : Pentane extraction (Total amount of oil in water)	1453
1974	Anderson <i>et al.</i>	1:9	Stirring : slow, 25 % oil vortex Flask : capped with aluminium foil Standing time : 1-6 hr	20	20 ± 2	Total petroleum hydrocarbon (API method No. 733-58) Saturated : Aromatics :	11620 10400
1980	Blackman & Law	1:9	Stirring : slow, 25 % oil vortex Aspirator: closed Standing time: 0-1 hr	24	19.5 ± 1.5	UVF : 360 / 310 nm IR : 2930 cm^{-1} (Calibration with fresh Kuwait crude oil)	650 - 100 3500 - 5800
1992	Sophia & Balasubramanian	1:9	Stirring : slow, 25 % oil Vortex Flask : capped with aluminium foil Standing time : 1-6 hr	20	20 ± 2	UVF : Details were not reported	1270
1994	This Study	1:100	Stirring : slow, 150 rpm Flask : closed tightly Standing time : nil	24	25 ± 1	UVF : Direct measurement on the aqueous phase (Calibration with diesel oil) DOC :	1900* 800-1000*

* See Table 2.6

results of Anderson *et al.* (1974), for the total petroleum hydrocarbon produced from an oil to water ratio of 1:9, were still higher. They determined the SWSF concentration by IR and found it to be 11620 $\mu\text{g L}^{-1}$, and by GC as 10400 $\mu\text{g L}^{-1}$.

In conclusion, the results of these studies cannot be directly compared due to the variation in the analytical methods used. Nevertheless, different ranges of SWSF concentration as mentioned above demonstrate the need for a standardised procedure, such as that devised in this study. The controlled and careful preparation conditions used in this study makes it advantageous quantitatively as well as qualitatively over those methods reported previously. In addition to being simple and practical it is adaptable for the preparation of SWSF from any light crude oil and possibly other oils as well (e.g. fuel oil). Stirring and temperature can be adjusted to different conditions if desired, various oil to seawater ratios are possible and various stock volumes can be obtained.

2.6 Conclusions

On the basis of the developmental work undertaken in the course of this study, it is concluded that the preparation of a homogenous seawater soluble fraction is not a simple process. The importance of considering contributory factors including stirring rate, temperature and reproducible sampling technique during the preparation of such a sensitive oil extract was explicitly demonstrated in the experiments carried out. The importance of optimising the analytical conditions when using UVF and DOC, especially the effect of heat, quenching and losses of volatiles has also been described.

As a result, a simple, practical and reliable method has been devised and optimised in

order to produce a saturated, stable and homogeneous SWSF of a crude oil in seawater. This required careful attention to a variety of factors, such as stirring rate, temperature and avoidance of loss of volatiles by performing the dissolution in a closed apparatus.

The dissolution of a Kuwait crude oil prepared by this procedure when monitored by two independent but complementary methods (i.e. UVF and DOC) was found to increase steadily over a 10 day period. Dissolution equilibrium was achieved using an oil to water ratio of 1:100 after 5 days of slow stirring (150 rpm) at $25 \pm 1^\circ\text{C}$. A general agreement between the two methods of analysis was demonstrated and provided an adequate means of monitoring the kinetics of oil dissolution. When compared to other studies, these concentrations were found to be within the range previously reported.

The dissolution method described here is particularly applicable to studies of the kinetics of oil degradation in water. However, the quantification of the photodegradation kinetics of SWSF requires accurate measurement of the concentration of individual hydrocarbon components and that can be made using GC-MS analysis.

CHAPTER THREE

CHAPTER THREE

CHARACTERISATION OF THE SEAWATER SOLUBLE FRACTION OF KUWAIT CRUDE OIL

3.1 Introduction

A typical analytical scheme for the characterisation of SWSF involves sample pre-treatment, extraction, fractionation and analysis steps (Figure 3.1). The precautions necessary to obtain representative, stable, homogeneous laboratory samples have been discussed in Chapter 2. Field samples may also require the addition of biocide, removal from light (e.g. dark glass containers), storage under cool conditions, use of air-tight all-glass sampling vessels and the addition of internal standards at an early stage after sampling. Obviously, attention should be given to sufficient replication and the use of 'blank' samples. A detailed discussion of this subject is outside of the scope of this thesis but the avoidance of contamination is of particular importance.

Contamination may arise from several sources during sample preparation. The most common contaminants are impurities in solvents, such as plasticisers, which could easily infiltrate the samples when they contact any plastics. Contamination by grease used for lubricating stopcocks in some glassware is also common if the glassware is not thoroughly washed and checked. Other sources of contamination are also possible. Denney *et al.* (1978) found trace amounts of organic contaminants in methanol extracts of samples stored in glass vials with Sn-Pb alloy foil-lined screw caps, which previously had been considered to be inert and non contaminating. These impurities were derived from the cork backing

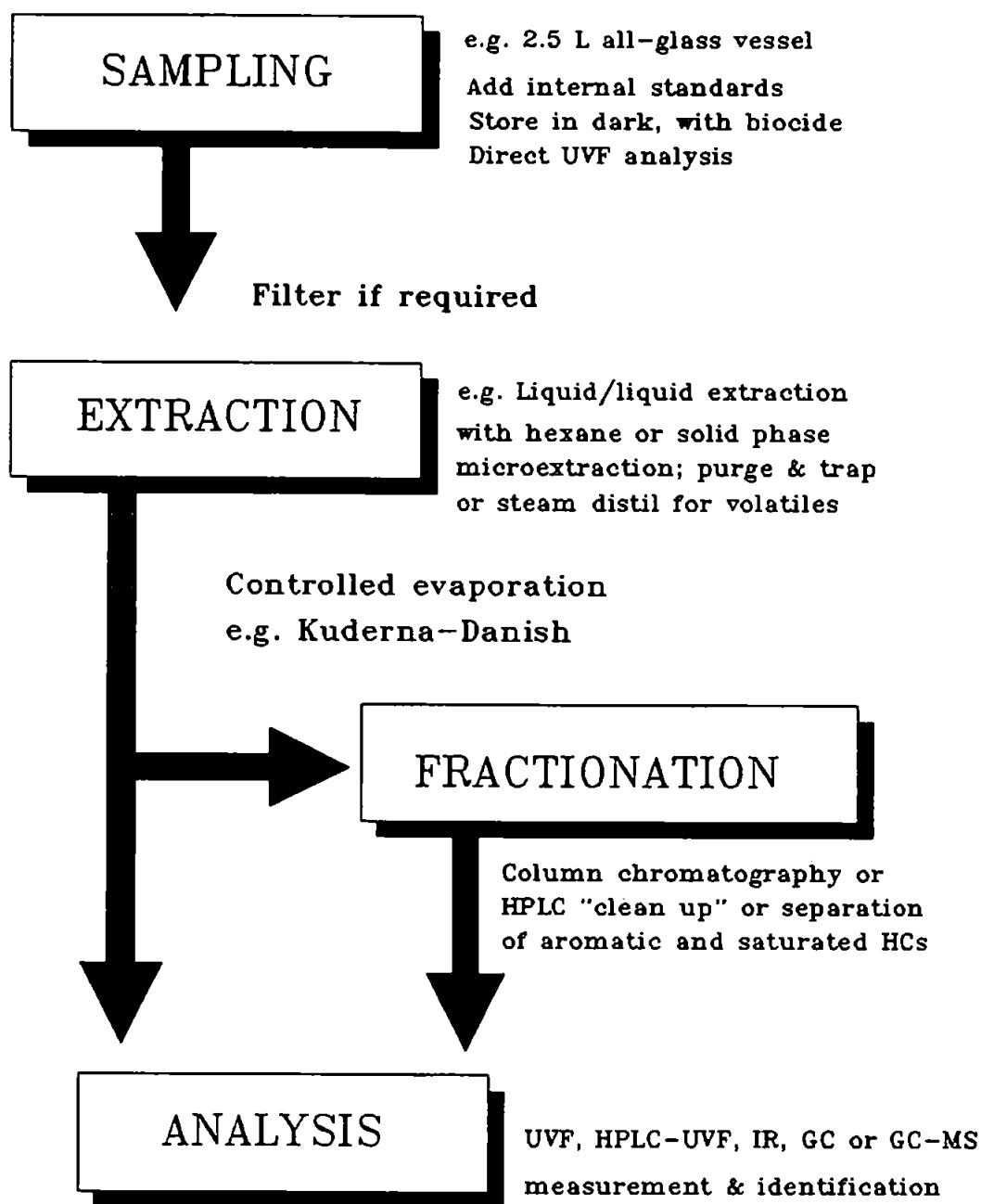


Figure 3.1 Analytical scheme for the characterisation of seawater soluble fraction (Rowland, 1994).

of the metal foil. Biedermann and Grob (1991) found "ghost" peaks overlapping the peaks of compounds under analysis. The components (such as squalene, cholesterol and wax esters) were found to arise from materials derived from the researcher's fingers when a glass stopper of an eluent reservoir was mistakenly touched.

Because of the high sensitivity of GC such contamination can easily cause severe problems even when the contaminants are present in low concentration. Thus, all sample processing hardware that could lead to GC artifacts must be routinely analysed to ensure the absence of detectable contamination.

3.1.1 Internal Standards

The preparation of SWSF samples should be followed by the early addition of suitable internal standards in a representative physical form (e.g. dissolved in water or adsorbed onto particulate matter, depending on the likely form of the analytes in the water). Ideally these should normally be deuterated analogues of the analytes to be measured. Such procedures have a long history of successful use in pharmaceutical analysis (e.g. drug metabolite studies). For most applications, deuterated analogues can be expected to have similar physical and chemical properties to the analytes but will have different molecular weight, mass spectral features and slightly different GC retention indices. This approach has been routinely applied in petroleum geochemistry by only a few researchers and only with GC-MS (e.g. Dahl *et al.*, 1985; Requejo, 1992; Peters and Moldowan, 1993). A variety of sources including an IOC/UNESCO (1982) manual recommend the use of deuterated naphthalene, biphenyl, anthracene and phenanthrene for the analysis of oil-in-water and for the quantification of polycyclic aromatic hydrocarbons (PAHs) after

photodegradation (Østgaard *et al.*, 1984; Behymer and Hites, 1985).

3.1.2 Extraction

Due to the low solubility of oil components in seawater an isolation and/or pre-concentration process is normally necessary before GC or GC-MS analysis. However, water soluble hydrocarbons have a wide range of volatilities and the techniques must allow for this to ensure adequate recovery. Techniques for the isolation of volatile and semi-volatile organics contained in aqueous phases can be broadly divided into liquid-liquid extraction (LLE), gaseous extraction, adsorption on solid sorbents and membrane processes (reviewed by Namiesnik *et al.*, 1990). A verification of the quantitative recovery of compounds of interest is required, whichever method is applied.

The isolation of hydrocarbons by LLE (both static and continuous) is one of the most widely used techniques due to its simplicity, speed and precision and was the method adopted here. It has been used with a large selection of solvents and *n*-pentane is generally recommended for use in LLE of SWSFs because of its low solubility in water, reasonable equilibration time and low chromatographic retention time. This makes the detection of even volatile water pollutants possible without solvent masking (Constable *et al.*, 1984). However, considerable volumes of solvent are used for extraction and so the extract must usually be preconcentrated to smaller volumes prior to analysis.

Solvent-free sample preparation methods for capillary chromatography using solid-phase micro-extraction have been recently developed (Otu *et al.*, 1993) and offer exciting possibilities for the future but, to date, these methods have not been applied widely.

3.1.3 Sample Concentration

A number of devices for concentrating solutions prior to chromatographic separation, have been described (for a review see Poole *et al.*, 1990). The methods used are summarised in Table 3.1 and include rotary evaporation (Grob and Müller, 1987), Kuderna-Danish evaporative concentration (White *et al.*, 1979), automated evaporative concentration (Ibrahim *et al.*, 1987), evaporation at room temperature (Bowers *et al.*, 1981) and gas blow-down methods (Constable *et al.*, 1984).

Some of the solvent reduction methods have been compared (Constable *et al.*, 1984; Grob and Müller, 1987); however, in practice the choice of method is often influenced by the availability of equipment, the time needed to concentrate each fraction, and the desired recovery of analytes. The latter in turn depends on the nature of the sample.

Unfortunately, the concentration of analytes in a sample extract is a potential source of large losses or variability in recovery during any analysis (Figure 3.2); however, some obvious precautions may alleviate this situation. For example, a safe procedure in any concentration system is avoiding evaporation to dryness. Ferreira *et al.* (1993) stated that for each concentration system there is a limit to the final concentration volume below which satisfactory recoveries are difficult to obtain.

Large (1991) and Grob and Müller (1987) reported that low-boiling point hydrocarbons (below *n*-decane or naphthalene) can be lost selectively during solvent removal by rotary evaporation, whereas Higgins and Guerin (1980) mentioned that diaromatic compounds such as naphthalenes and biphenyls were lost during concentration in a nitrogen blanket

Table 3.1 **Methods used for solvent reduction**

Method	Principle	Comments
Rotary evaporation	Solvent removed at reduced pressure by mechanically rotating a flask in a controlled-temperature water-bath. Provision is made for condensing and collecting the evaporated solvent.	Volatile compounds are generally lost. Recovery of less volatile material may be lower than expected owing to entrainment of the sample in the solvent vapour. Adsorption on the glass walls of the flask and apparatus may be a problem. Uncontrolled expulsion from the flask due to uneven evaporation may occur.
Kuderna-Danish evaporative concentrator	Evaporative concentrator is operated at atmospheric pressure under partial reflux conditions using a three-ball Snyder column with an efficiency of about 2.7 theoretical plates. Condensed vapour in the Snyder column is returned to the boiling flask, washing down organics from the sides of the glassware. The returning condensate also contacts the rising vapour and helps to recondense volatile organics. The concentrator is mounted with the boiling flask in a controlled-temperature water-bath and the final solvent concentrated into a collection tube of small volume compared with the boiling flask.	Provides a slower rate of evaporation than the rotary evaporator but recovery of trace organic compounds is generally higher. Generally not possible to reduce sample volume of several hundred millilitres to less than 1 mL in a single apparatus.
Automated evaporative concentrator (EVACS)	Solvent from a pressure-equalized reservoir is fed at a controlled rate into a concentration chamber where the solvent is vaporized through a short distillation column. Nitrogen gas in the absence of heat is used to complete the concentration to <u>ca.</u> 1 mL.	Requires a boiling difference of <u>ca.</u> 50 °C between solvent and analyte for high recovery. Allows recovery of solvent and incorporates liquid level monitors for unattended operation.
Gas blow-down	A gentle stream of pure gas is passed over the surface of the extract contained in a conical-tipped vial or culture tube partially immersed in a water-bath. The solvent evaporation is a function of the gas flow-rate, the position of the gas inlet tube relative to the refluxing solvent, the water-bath temperature and the solvent surface area.	Generally limited to sample volume < 25 mL. High gas flow-rates may cause sample losses by nebulisation. Gas supply may contaminate sample. If sample is reduced to dryness, subsequent dissolution may be incomplete. Carryover of aqueous and high-boiling solvents difficult to remove by evaporation.

(Source: Poole *et al.*, 1990)

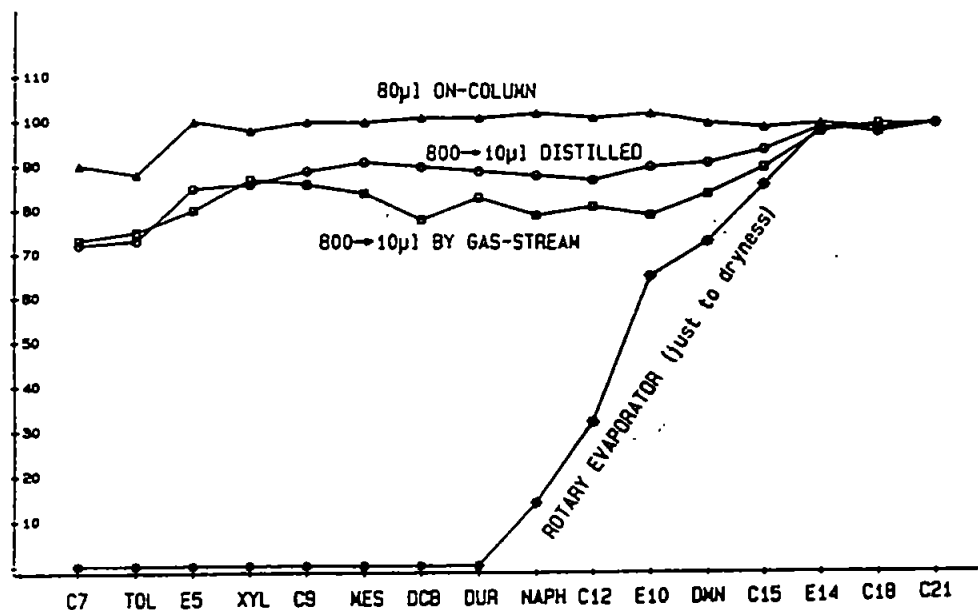


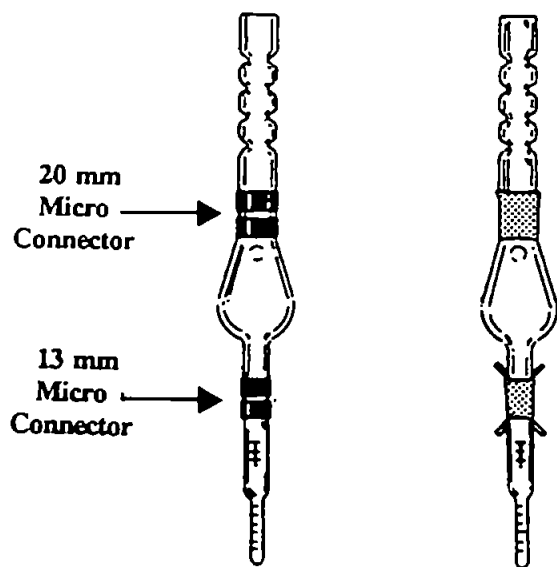
Figure 3.2 Recovered solute material after reconcentration by a factor of 80, using various solvent evaporation techniques (average of at least three determinations). A value of 100 on the vertical axis indicates no loss during solvent evaporation. Solutes are listed as eluted from an apolar column. Solvent evaporation carried out column-internally, i.e., upon on-column injection of an 80- μ L volume, by distillation, evaporation using a stream of nitrogen and a complete evaporation using a rotary evaporator (Grob and Müller, 1987).

and reduced pressure apparatus. Even the inert atmosphere and the low temperature inherent with the use of such a concentration system did not aid the recoveries. The same researchers developed an evaporative concentrator used with absorbent materials in an attempt to enhance the recoveries of the diatomics. However, although recoveries ranged from 62% to 90% depending on the final concentration volume, problems encountered with the absorbents remained the main disadvantage. Alternatively, Price and Carlson (1981) used a controlled-rate evaporator which combines heating and nitrogen flow for a thousand-fold concentration of fatty acids. Although the recoveries were, in general, more than 70%, special glassware and a high flow rate of nitrogen were required.

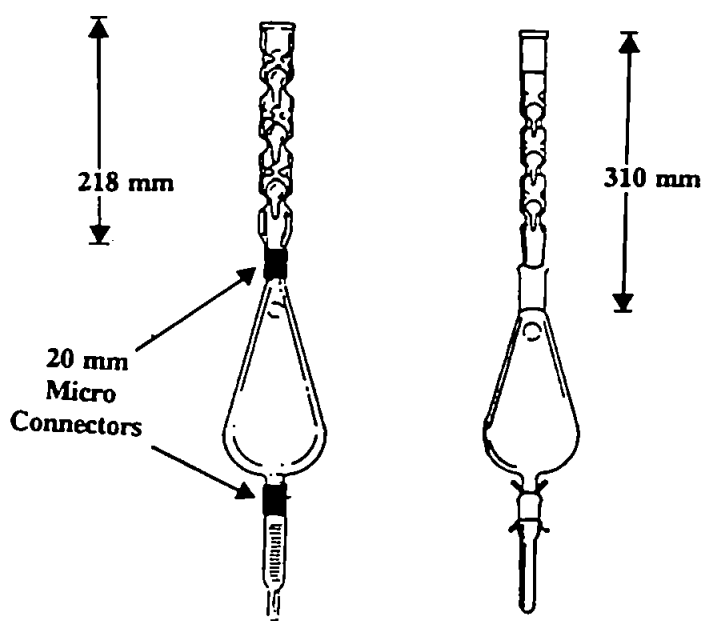
An alternative method to both rotary evaporation and nitrogen blow down is the Kuderna-Danish (K-D) evaporative concentrator. K-D has been adapted for use by the Standing Committee of Analysts (SCA) (e.g. SCA, 1987) for examination of oil-in-water and associated materials and is widely used in the trace analysis of pesticides in water (Chau and Lee, 1982).

The apparatus is available in two sizes termed micro- and macro- systems (Figure 3.3). The K-D concentrator can be equipped with either a condenser or a Snyder column and operates by solvent distillation. In this method, the solvent (40-60% of normal flask capacity) is distilled through a Snyder column and the sample concentrates in a small volume reservoir attached to the bottom of the evaporator vessel. The apparatus is heated in a controlled-temperature waterbath and can provide final concentrates of 2 mL or less.

The micro K-D concentrator is capable of reducing 30-40 mL of solvent to less than 2 mL (10 μ L - 2000 μ L) in a single step. This simple three-piece apparatus has been compared



Micro Kuderna-Danish Concentrator



Macro Kuderna-Danish Concentrator

Figure 3.3

The Kuderna-Danish apparatus used for concentrating materials dissolved in volatile solvents.

with a more complex but automatic evaporative concentration system (EVACS) and recoveries were found to be the same or slightly better (Ibrahim *et al.*, 1987). A recent apparatus combining a K-D concentrator with a continuous extraction apparatus in one device has been produced commercially (DeGraff, 1992). This method may prove to be attractive for the analysis of volatiles because it appears to eliminate losses caused by transfer steps during preparation.

Since the K-D concentrator is operated at ambient pressure, the rising vapour must build up sufficient pressure to force its way past the condenser stage. Since the vapour is slow to work its way through the different stages of the condenser, there is initially a large amount of vapour condensation that returns to the bottom of the apparatus. The returning condensates continuously wash down organics from the side of the glassware. This also helps to recondense volatile organics when they contact the rising vapour. Although this process is slower than the rotary evaporation method, higher recoveries of trace organics are obtained (Karasek *et al.*, 1981).

Combining concentration techniques such as the K-D concentrator, that concentrate to a few millilitres, with the use of a stream of inert gas or dry air for final concentration, has been found to be most effective in many cases. These include the concentration of pesticide extracts (Chau and Lee, 1982) and the determination of very low concentrations of hydrocarbons and halogenated hydrocarbons in water (Standing Committee of Analysts, 1987).

Several factors influence the efficient performance of the K-D. To ensure quantitative results, Ripley and Chau (1982) recommended use of low boiling point solvents (such as

dichloromethane or pentane) for extraction to eliminate the need for higher temperatures during evaporation with the K-D concentrator. Higher boiling point solvents also required longer concentration times leading to high losses during pumping.

Ferreira *et al.* (1993) evaluated the accuracy of the micro K-D concentrator during the concentration of a mixture of alcohols with boiling points ranging from 120 °C to 270 °C. They found that more concentrated solutions showed less losses than more diluted solutions. The latter were found to be more affected at lower final volumes. However, addition of larger amounts of solutes to increase the concentration of the solution and using medium boiling point solvents such as ethanol or propan-2-ol at the final stage of concentration also reduced losses.

Greater losses generally occur if solvents are reduced to volumes below (*ca.*) 1 mL, although it was found that 0.5 mL was a safe volume for concentrating a solution containing 1 µg pesticides in 10 mL of benzene or petroleum ether in a micro K-D apparatus (Chau and Lee, 1982). Ferreira *et al.* (1993) have found that the amount of sample recovered also depends on the shape of the collection tube. A conical receiving vessel with a large internal diameter performed better than a cylindrical vessel because the boiling process became less violent. Junk *et al.* (1974) compared the recovery of volatile hydrocarbons using a number of concentration vessels of different shapes and sizes. They also concluded, that the most effective vessel shape is that in which the solution has a large exposed surface area to prevent violent eruption during concentration.

To achieve better quantification results, Ferreira *et al.* (1993) recommended the use of internal standards which cover the entire range of solute boiling points (at least 3) and use

of a wide receiving flask.

3.1.4 Analysis

Once the sample has been extracted and concentrated, a detailed analysis and quantitative characterisation is necessary. Several methods are available but gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) techniques are the preferred methods for SWSFs of crude oil. GC-MS, in particular, combines the high resolving power of GC with sensitivity sufficient for the detection of nanogram amounts of individual hydrocarbons in complex samples and provides detailed mass information about individual GC peaks. The introduction of cryogenically cooled GC or GC-MS is particularly useful for the analysis of SWSFs because it allows even the most volatile components to be determined quantitatively. Thus it provides a more accurate estimate of the content of SWSF solutions.

Qualitative and quantitative analysis by GC has been the subject of many published reports. General aspects are detailed by Debbrecht (1985) and Umbreit (1985), whilst petroleum and petrochemical analysis are covered by Smith and Paulsen (1985) and reviewed by Rowland and Revill (1994). Analysis of SWSF of crude oils is discussed by Murray *et al.* (1984). Similarly, quantification and identification of petroleum compounds using GC-MS has been reported in studies of biomarkers (Dahl *et al.*, 1985; Requejo, 1992) and of oil-in-water (Albaiges and Albrecht, 1979; Østgaard *et al.*, 1984; Requejo and Boehm, 1985; reviewed by Rowland, 1994). There are also many reports of the employment of GC-MS in the quantification of the photodegradation of oil hydrocarbons and identification of the photo-products (Ehrhardt and Petrick, 1985; Ehrhardt *et al.*, 1992;

Burns, 1993).

3.2 Aims

The main objective of the work described in this chapter was to determine qualitatively and quantitatively the individual compounds present in the SWSF of a Kuwait crude oil.

Specifically the objectives were:

1. Optimization of analytical procedures for sample extraction, extract concentration, storage of concentrates awaiting analysis, and analysis.
2. Application of the optimised analytical procedures for work-up of SWSF samples in order to quantitatively identify individual components in the SWSF prior to photodegradation.

3.3 Experimental

The work described in this section was undertaken to achieve the objectives stated earlier i.e. to optimise and to assess the analytical methodology procedures for the work-up of SWSF samples and their analysis by GC and GC-MS. The assessment of the analytical methodology included:

- (1) Checking the reproducibility of GC on-column injection used in the analysis of K-D standard solution and SWSF compounds.

- (2) Validating the K-D evaporative concentrator for the recoveries of deuterated standards and oil hydrocarbons and determining the percentage recoveries.
- (3) Optimising the volume of final concentrate and the amounts of deuterated internal standards required for the quantitative analysis.
- (4) Investigating sample storage conditions after preparation.
- (5) Verifying possible contamination from glassware and other sources during sample work-up and analysis.

Once the analytical procedures were optimised they were used to obtain quantitative and qualitative information about the individual SWSF components of Kuwait crude oil.

3.3.1 Materials

Chemical standards including deuterated benzene, naphthalene and phenanthrene were purchased from the Aldrich Chemical Co. Ltd., U.K., with a purity grade of 98%. The following authentic alkylbenzenes were kindly supplied by Dr. Walter Hartgers, Organic Geochemistry Unit, Delft University of Technology, The Netherlands: 1,3-dimethylbenzene; 1-ethyl-2-methylbenzene; 1-ethyl-3-methylbenzene; 1-ethyl-4-methylbenzene; 1-isopropyl-2-methylbenzene; 1-isopropyl-3-methylbenzene; 1-isopropyl-4-methylbenzene; 1-methyl-2-propylbenzene; 1-methyl-3-propylbenzene; 1-methyl-4-propylbenzene; 1,2-dimethyl-3-ethylbenzene; 1,2-dimethyl-4-ethylbenzene; 1,3-dimethyl-2-ethylbenzene; 1,3-dimethyl-4-ethylbenzene; 1,4-dimethyl-2-ethylbenzene.

The remaining commercially available authentic C₃ and C₄ alkylbenzenes and *n*-alkanes were purchased from Aldrich Chemical Co. Ltd., U.K.

Brent crude oil was obtained from the Warren Spring Laboratory, Stevenage, U.K., in a sealed stainless steel container.

Micro Kuderna-Danish evaporative concentrators were purchased from Aldrich Chemical Co. Ltd., U.K., including a 112 mm micro condenser, 40 mL flask and 2 mL receiving vessel graduated from 0 to 0.3 mL in 10 μ L units, at 0.4 mL and 0.5 to 2 mL in 100 μ L units. A macro Kuderna-Danish evaporative concentrator was provided by Zeneca, Brixham, U.K. This comprised 218 mm 3-ball Snyder column, 500 mL flask and 15 mL receiving vessel. The receiving vessel was graduated in 0.1 mL units to 4 mL, at 5 mL and 0.5 mL units from 6 mL to 15 mL.

Syringes (5 μ L capacity) used for GC analyses were purchased from Scientific Glass Engineering (SGE) and vials used for sample storage were purchased from Aldrich Chemicals Co. Ltd., U.K.

Preparation of SWSFs

The experimental procedure for preparing SWSFs was as described in Chapter 2, Section 2.4.2. SWSFs were prepared so as to provide sufficient samples for the identification and quantification of constituents and for the photodegradation experiments. For this, the oil and seawater was left to stir for 5 days after which the stirring was stopped and the aqueous phase collected carefully in a precleaned 1 L flask.

3.3.2 Extraction and Extract Concentration of SWSF Samples

For quantitative analysis, SWSF samples (50 mL) were extracted with *n*-pentane (2 x 5 mL) in a 100 mL all glass separatory funnel after the addition of 100 μ L of *n*-pentane containing 50 μ g benzene- d_6 , 50 μ L of *n*-pentane containing 10 μ g naphthalene- d_8 and 50 μ L of *n*-pentane containing 5 μ g phenanthrene- d_{10} internal standards. The extract was dried by passing through a column (Pasteur pipette) of pre-extracted cotton wool and anhydrous sodium sulphate. For qualitative analyses (identification of SWSF compounds), 90 mL of the SWSF solution was extracted and dried as above.

The SWSF extracts were concentrated to less than 1 mL using a controlled micro K-D concentrator (procedure is described in Section 3.3.10), transferred to small vials and a final volume of 0.3 mL was obtained by evaporation with a gentle stream of nitrogen.

3.3.3 Measurement of the Recoveries of Internal Standards

To calculate the recovery of the deuterated internal standards added to SWSF samples, a solution of 50 μ g of benzene- d_6 , 10 μ g naphthalene- d_8 and 5 μ g phenanthrene- d_{10} was prepared in 0.3 mL *n*-pentane and analysed under the conditions used for analysis of the SWSF samples. The integrated peak areas of the internal standards obtained from two analyses were compared and the percentage recoveries calculated.

3.3.4 Retention Indices of Authentic Benzene Reference Compounds

To identify the different isomers of alkylated benzenes in the SWSF, the available

alkylbenzenes were analysed and their retention indices (RI) were calculated. RI values are based on a comparison of the retention time of the compound of interest with those of reference standards included with the solutes. Both Kovàts and Lee methods are used (Kovàts, 1958; Lee *et al.*, 1979). RI of the authentic compounds and SWSF compounds were calculated according to Kovàts method but with a non-isothermal temperature programme similar to the approach of Hartgers *et al.* (1992).

Solutions of appropriate concentrations of all the available C₃ and C₄ alkylbenzenes (26 compounds) were individually prepared in *n*-pentane. An aliquot of each solution was individually mixed with an aliquot of an *n*-alkane mixture (C₆-C₁₂) and analysed by cryogenically cooled GC-MS using a non-isothermal temperature program of the GC (see instrumental methods, Section 3.3.14). Retention indices (RI) were calculated from the equation:

$$RI = 100N + 100n \left\{ (R_x - R_N) / (R_{N+n} - R_N) \right\}$$

where R_x , R_N and R_{N+n} are the retention times of the compound and *n*-alkanes containing *N* and *N+n* carbon atoms, respectively.

3.3.5 Retention Indices of SWSF Compounds

Aliquots of the concentrated extracts of the SWSF samples were mixed with aliquots of an *n*-alkane mixture (C₆-C₂₅) and analysed as above by cryogenically cooled GC-MS. Retention indices were calculated as above.

3.3.6 Identification of SWSF Compounds and Analysis of Blanks

Identification of the C₃ and the C₄ alkylbenzenes in SWSF was made by comparing their RI with those obtained for authentic compounds. The C₂ alkylbenzenes were identified by comparison with the RI reported by Hartgers *et al.* (1992).

Identification of the alkylnaphthalenes (C₂-C₃) was made by comparing RI with those of isomers in the crude oil or the authenticated distributions found in the literature (e.g. Alexander *et al.*, 1983; Rowland *et al.*, 1984; Volkman *et al.*, 1984; Rowland *et al.*, 1986; Radke, 1987). The remaining compounds were identified by comparison with those in the NBS computerised GC-MS library, or by comparing with spectra reported in the literature.

To identify components which could originate from the solvent or from the seawater, two blanks were included in the analysis. A solvent blank (30 mL *n*-pentane) was concentrated by K-D and N₂ blow down to 0.3 mL (100 fold concentration) and a seawater blank (50 mL) spiked with the same amount of internal standards used for quantifying the SWSF samples (i.e. 50 µg benzene-d₆, 10 µg naphthalene-d₈ and 5 µg phenanthrene-d₁₀) and prepared as described above. Both blanks were analysed under the conditions used for SWSF samples for comparison.

3.3.7 Quantitation of SWSF by GC-MS

Peaks of the individual identified SWSF compounds obtained from the GC-MS analysis were integrated twice:

1) By plotting the reconstructed total ion abundance, then integrating the area of each peak on the total ion chromatogram (TIC). This method provided the total intensities of all the ions associated with each component peak.

2) By plotting the mass chromatogram (MC) of only one selected ion, characteristic for each compound or compound class, and then integrating the peak area for that ion. For this, the molecular ions were used. This method provided the intensity of only the specific ion selected for each compound.

Areas of isomers which were either co-eluting or partially resolved were integrated as one peak. The concentrations of SWSF compounds integrated by either method were calculated with reference to the deuterated internal standards which were integrated using the MC method. The molecular ions of the deuterated standards used were m/z 84 for benzene- d_6 , m/z 136 for naphthalene- d_8 and m/z 184 for phenanthrene- d_{10} . This method was used because the deuterated standards were not always separated by GC from the corresponding non-deuterated compounds. Calculations of concentrations were made by calculating the ratio of peak areas of the internal standards and SWSF compounds versus amount of IS added. Benzene- d_6 was used for (C_0 - C_4) alkylbenzenes; naphthalene- d_8 for (C_0 - C_3) alkylnaphthalenes and phenanthrene- d_{10} for phenanthrene and remaining analytes. These three internal standards thus covered the whole GC retention range of compounds present in the SWSF and provided a better quantitative approach than using only one internal standard.

The concentrations of SWSF compounds obtained by the MC method were also compared with the concentrations in the original oil obtained using the same method.

3.3.8 Analysis of Asphaltene-Free Kuwait Crude Oil

To calculate the partition coefficient of individual components identified in the SWSF, the concentration of each component was determined in the crude oil. Resins and asphaltenes were quantitatively removed from a sample of the oil to produce asphaltene-free oil for GC-MS analysis. The separation of these fractions was carefully carried out to minimise losses of volatiles so as to allow quantitative comparison of selected compounds in the crude oil with their concentration in the SWSF. Whole crude oil (9.1 mg) was dissolved in *n*-pentane (1 mL) containing benzene- d_6 (50 μg), naphthalene- d_8 (10 μg) and phenanthrene- d_{10} (5 μg) internal standards in a capped vial. The asphaltenes were allowed to precipitate for 15 minutes in the refrigerator before the *n*-pentane soluble fraction was pipetted into a clean vial and analysed by cryogenically cooled GC-MS under the same conditions used for SWSF. The asphaltenes fraction was dried under a gentle stream of N_2 and weighed. Peak areas of the oil components and internal standards were integrated from the mass chromatograms (MCs) constructed from the molecular ions and were quantified by comparing compounds and standards.

3.3.9 Reproducibility of On-Column Injection

To examine the reproducibility of on-column injection for both peak heights and peak areas for the determination of SWSF, standard solutions of naphthalene- d_8 (80 $\mu\text{g mL}^{-1}$) and phenanthrene- d_{10} (80 $\mu\text{g mL}^{-1}$) in *n*-pentane were tested. This was made by injecting 0.5 μL eight times into a GC (see instrumental methods below). Both peak areas and peak heights were obtained and relative standard deviations (RSD) calculated.

3.3.10 K-D Concentration

There is very little literature available on how to use the K-D apparatus to concentrate an extract. The short instructions available (mainly found in catalogues advertising this apparatus) are vague and insufficient. According to these sources, the flask is to be "charged with material to about 40% to 60% of normal capacity and to set the assembly up over a hot water bath. Heavier fractions will reflux and concentrate in the receiving vessel". However, when the concentrator was first used following these instructions, no concentration was achieved even after 2 days of continuous operation. A similar procedure is given in a method of the Environmental Protection Agency (EPA), but this instructs the user to concentrate the extract over a water bath of 100 °C, for solvents such as dichloromethane or *n*-hexane. This is capable of causing severe losses for volatiles and only minimal recovery of semivolatiles.

However, after several manipulations of the apparatus and attempts to concentrate the extract, the procedure described in the following sections was finally optimised and adapted.

Two types of materials were tested:

- 1) Standard solutions of deuterated benzene, naphthalene and phenanthrene, between 10 and 80 $\mu\text{g mL}^{-1}$, prepared in different organic solvents;
- 2) Solutions of fresh Brent crude oil (2 mg mL^{-1}) spiked with deuterated naphthalene and phenanthrene standards (20 $\mu\text{g mL}^{-1}$ each) prepared in DCM for the recoveries of C_9 to C_{11} *n*-alkanes and the deuterated standards.

The following set of factors were analysed throughout the K-D validation: type and amount of material; type of solvent; water bath temperature; final concentration volume; duration of concentration; size of K-D apparatus; and manipulation of apparatus (e.g. use of insulation).

The first task was to improve upon the initially poor performance of the K-D apparatus. It was found that this could only be achieved by wrapping the whole apparatus except the receiving vial, which is immersed in the water bath, with aluminum foil and cotton wool.

An investigation was carried out to optimize the temperature and also to reduce the duration of the concentration while retaining good sample recovery. Temperatures between 40 to 100 °C were tested, the time of reduction at each temperature was recorded and recovery of the deuterated standards was determined.

The investigation also included the use of solvents of different boiling points namely *n*-pentane, *n*-hexane and DCM which were spiked with increasing amounts of the material tested. Concentration to a different final volumes was examined for differing recovery amounts. A macro K-D concentrator was compared to a micro K-D concentrator using the same concentration procedure.

Final volumes obtained from the various tests were then quantitatively transferred to small vials and analyzed either by GC or by cryogenically cooled GC-MS (see instrumental methods Section 3.3.14).

Optimised Procedure for K-D Concentration

The experimental setup of the K-D concentrator is shown in **Figure 3.4**.

1. A water bath was prepared and adjusted to the temperature required. A thermometer was kept in the water bath to constantly monitor the temperature.
2. The K-D concentrator was first rinsed with the solvent to be tested, then filled with 30 mL of the same solvent.
3. The solvent was spiked with an aliquot of the standard solution or crude oil solution, then gently swirled. An antibumping granule was added.
4. The apparatus (except the part immersed in the water) was then wrapped with cotton wool and aluminum foil for insulation.
5. The apparatus was then held in a laboratory stand over the water bath while keeping the receiving vessel fully immersed in water. A gently boiling organic solvent solution should be maintained.
6. When the solvent volume was reduced to about 2 mL it had to be constantly monitored to avoid over boiling.
7. When the solvent had been concentrated to the volume required, the K-D was removed from water bath and allowed to cool on the bench or, preferably, by running cool water over the concentrator vessel to speed up the cooling and to reconcentrate the vapour. The returning condensate washes down any solute residues from the glass walls into the receiving vessel.
8. The concentrate was transferred quantitatively to a small pre-rinsed vial and the volume recorded.
9. The concentrate was then analysed under the same conditions which had been used before concentration.
10. Integrated peak areas for each compound were then obtained to enable the

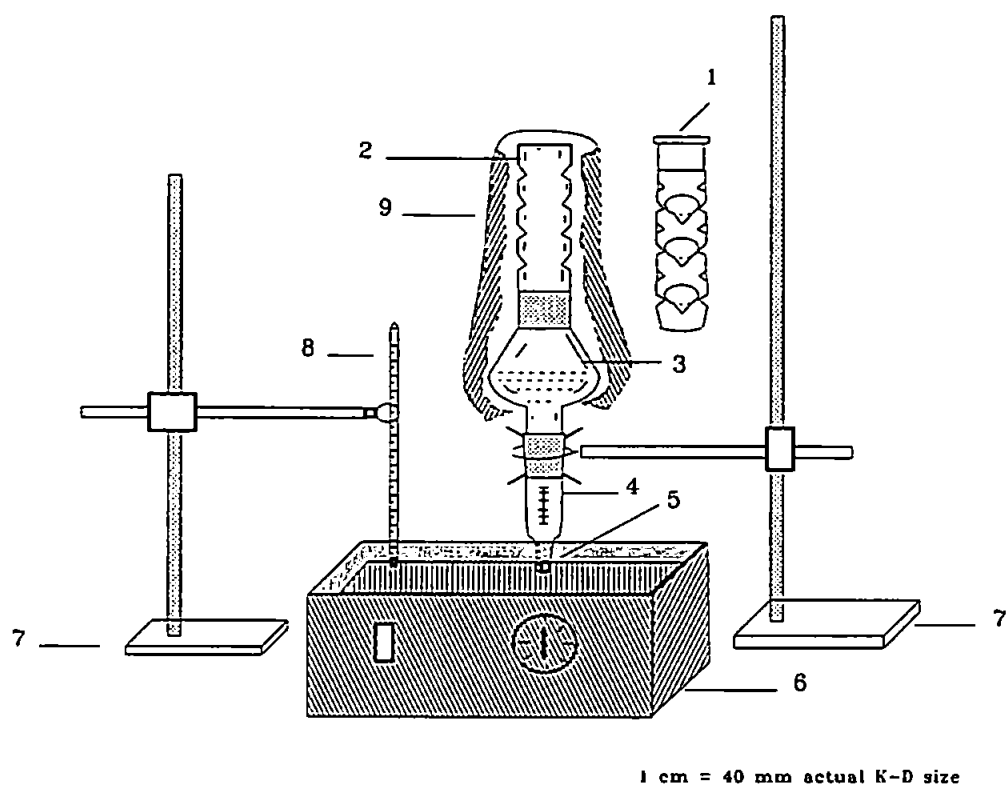


Figure 3.4 The experimental setup of K-D concentrator. 1= Snyder column; 2= micro condenser, 112 mm; 3= flask, 40 mL; 4= receiving vessel, 2 mL; 5= boiling chip; 6= water bath; 7= laboratory stand; 8= thermometer; 9= aluminium foil and cotton wool wrap.

calculation of recoveries both before and after concentration.

3.3.11 Optimizing Volume of Final Concentrate and Amount of Deuterated Internal Standards

To ensure reliable quantitative analyses of SWSF before and after photodegradation, the volume of the final concentrate for GC-MS analysis that provided sufficient sensitivity for the detection of SWSF components present in low concentration was determined. This was carried out by concentrating a SWSF extract to 1 mL and then further to 0.3 mL. GC analysis was made for both volumes and the peak areas obtained from both concentrates were compared for optimal response.

The amount of deuterated internal standards required to be added to SWSF samples before extraction was also optimised. This was carried out by spiking SWSF samples with various amounts of deuterated benzene, naphthalene and phenanthrene. After extraction and reconcentration the peak areas of the deuterated compounds were compared with the peak areas of the non-deuterated compounds in the SWSF and the optimum amount of internal standards were consequently determined.

3.3.12 Storage of SWSF Concentrates After Extraction and K-D Reconcentration

The conditions under which SWSF concentrates are stored are important if volatiles are not to be lost. Solvents can alter the integrity of samples by co-evaporation with consequent variation in concentration. Therefore, losses of solvent were measured to

determine the optimum storage conditions.

Two types of sample storage vials were tested: a 1.5 mL Wheaton screw-cap vial with an 8-425 screw-cap (type 1) and a 1 mL Wheaton glass serum bottle with an 11 mm (o.d.) mouth (type 2). The vials were filled with 0.5 mL of *n*-pentane chosen because it was the volume routinely used for sample analysis and *n*-pentane was the most frequently used solvent for sample preparation. Changes during storage were determined by weight, using a balance accurate to 5 decimal places (Mettler AE160, European Instruments, U.K).

Vials (type 1) were either; capped tightly and left on the laboratory bench at room temperature; capped tightly with an aluminium foil liner and left on laboratory bench; capped tightly and stored at -20 °C or capped tightly with an aluminum foil liner and stored at -20 °C.

Vials (type 2) were either; capped and left on the laboratory bench at room temperature; capped and stored at 4 °C or capped and stored at -20 °C.

Measurements were taken over a period of 54 days of storage. Before any measurement was taken, vials were taken out of the refrigerator or freezer, left in a dark, cool place for a few minutes to adjust to room temperature, dried then weighed.

3.3.13 Verification of Possible Contamination of Samples

Preliminary work revealed the presence of persistent contamination which appeared on the gas chromatograms and interfered with the analytes of interest. Sources which could have

given rise to this problem were investigated.

Potential sources of contamination include: inadequately washed glassware; solvents or solvent storage bottles; rotary evaporators and K-D used to concentrate solvents; N₂ used to reduce solvents; and GC syringes. Table 3.2 summarises suspected sources of contamination and the methods used to investigate each. An examination of each source was made systematically and sequentially. Additionally, examples of some contaminants that can come in contact with SWSF samples during preparation, handling or analysis were selected and *n*-pentane extracts were qualitatively analysed by GC-MS. These samples included silicon grease, pipette fillers, gloves, 'Suba.Seal' and PTFE tape. Mass spectra were obtained to aid the identification. Prior to any analysis, solvent blanks and a standard mixture of *n*-alkanes were routinely chromatographed (GC) to check the performance of the analytical GC columns.

3.3.14 Instrumental Methods

Gas Chromatography (GC)

GC analyses were performed with Carlo Erba Mega 5300 series instrument fitted with a flame ionisation detector. The GC oven was fitted with a 30 m x 0.32 mm i.d. (0.25 µm film thickness) DB-5 fused silica column (J&W, U.K) and on-column cold injector. The oven temperature programme used for on-column reproducibility injection tests and for verification of sample contamination was from 40 °C to 300 °C at 5 °C min⁻¹ and 10 min hold at 300 °C. The carrier gas was hydrogen at a flow rate of 2 mL min⁻¹ measured at 250 °C. Chromatograms and peak areas were obtained by a Shimadzu-C-R3A Chromatopac computing integrator.

Table 3.2 Examination of potential sources of contamination during sample work-up.

Suspected Contamination source	Examination carried out
Glassware washing	<p>Methods of glassware washing which were tested were :</p> <p>1) Soaking glassware in a solution of Decon 90 in a glass tank, followed by hot tap water rinse then several distilled water rinses. Finally soaked in deionised water for 2 hr.</p> <p>2) Soaking glassware in chromic acid solution, followed by distilled water rinse, soaked for 2 hr in deionised water. Glassware was then dried in an oven at 120 °C overnight. When cooled, selected glassware (mainly items used for sample extraction) were tested.</p>
Glassware	<p>Selected glassware from the two methods of washing were examined by rinsing 3 times with 10 mL solvent and concentrating the rinse by rotary evaporator or K-D to < 1 mL.</p>

"continued..."

Table 3.2 "continued"

Suspected contamination source	Examination carried out
Rotary evaporator and K-D concentrator	Comparison of two rotary evaporators and two K-D concentrators were made using a pre-checked glassware to determine if these routinely used concentration apparatus were contaminated.
N ₂ gas	A comparison was made using concentrates obtained by rotary evaporation alone, and by rotary evaporator and N ₂ to the same volume.
Storage vials	To avoiding transferring to the storage vial, the concentrates were directly analysed from the flask used in the rotary evaporation.
Solvents and solvent storage bottles	A comparison was made using solvents stored in bottles for temporary use, and directly from a Winchester stock bottle.
GC syringe	A comparison of two syringes was made to determine if the syringe routinely used was contaminated.

Gas Chromatography-Mass Spectrometry (GC-MS)

A Hewlett-Packard 5870 with chilled autosampler and cryogenic cooling of the GC oven was fitted with 12 m x 0.2 mm (0.33 μm film thickness) HP1 fused silica column (Hewlett Packard, U.K). The chilled autosampler was used in order to maintain the sample at a constant temperature (15 $^{\circ}\text{C}$) before it was analysed. The oven temperature program used for K-D recovery tests, quantification and calculation of RI of SWSF components was from -20 $^{\circ}\text{C}$ to +300 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C min}^{-1}$ and 5 min hold at 300 $^{\circ}\text{C}$. The injection temperature was 250 $^{\circ}\text{C}$ and injection (1 μL) was made automatically in the splitless mode. Helium was used as the carrier gas. Electron impact spectra were obtained at 70 eV under the following conditions; cycle time 1.2 s; resolution 1000; and mass range of 35-800 Daltons for full spectral acquisition.

3.4 Results and Discussion

3.4.1 Reproducibility of On-Column GC Injection

The RSD in peak area and peak height for 8 injections of naphthalene- d_8 were 4.4% and 5.4%, respectively (Table 3.3). For phenanthrene- d_{10} the RSD of peak area and peak height were 5% and 7.4% respectively. Gough (1989) reported a GC reproducibility of *ca.* $\pm 6\%$ for peak areas of replicates (10x) made by on-column analyses of a hydrocarbon mixture. However, the variability in the data obtained here from the replicate (8x) GC analyses could be instrumental or technical in nature. In general terms, the size of a chromatographic peak is proportional to the amount of analyte contributing to that peak.

Table 3.3 Reproducibility of on-column injection of deuterated naphthalene and phenanthrene

naphthalene-d₈		
Injection No.	Peak Area Automatic Integral (Unit)	Peak Height (mm)
1	192256	31
2	201538	35
3	197062	35
4	184172	32
5	194484	33
6	198868	35
7	175913	31
8	189235	32
Mean	191691	33
S.D. (n-1)	8425	1.8
R.S.D	4.4 %	5.4%
phenanthrene-d₁₀		
1	251635	33
2	263735	39
3	271928	41
4	253409	38
5	259275	38
6	275211	41
7	233945	35
8	261312	38
Mean	258806	37.9
S.D. (n-1)	12932	2.8
R.S.D	5 %	7.4 %

Carlo Erba Mega 5300 series GC; DB-5 column; 5 µL GC syringe; GC oven temperature: 40 - 300 °C at 5 °C min⁻¹, Carrier gas: Hydrogen.

Thus peak sizes are influenced by injection volume and error could be introduced should the injection volume differ. Variability could also result from differences in injection time and initial temperature of the GC column. Temperature can influence retention time by approximately 3% °C⁻¹. A 1 °C change in column temperature can cause a 3% change in retention time and thus 3% change in peak width (see Debbrecht, 1985). Thus as mentioned by Debbrecht (1985), to maintain analysis at 1% accuracy, the temperature of the column must be controlled with ± 0.3 °C and preferably to better than 0.1 °C, assuming the temperature change of the column to be the only factor producing error. Brindle and Xing-Fang (1990) found that the initial temperature of analysis affected the quantification of PAHs including naphthalene and phenanthrene. Their work indicated that, depending on the solvent used, the largest response as determined by peak area and peak height was between the boiling point of the solvent and 10-20 °C higher than the boiling point.

Reproducibility of peak height and peak width is also dependent on the reproducibility of sample injection time. Debbrecht (1985) mentioned that this is especially important on early eluting narrow peaks where the peak is controlled by injection time rather than the chromatographic process. Therefore, considering the influence of these factors on the reproducibility of GC analyses, the results as achieved here showed that the reproducibility of on-column injection was satisfactory, RSD of peak areas was $\leq 5\%$. Peak areas were therefore used in determination of analyte concentrations when required.

3.4.2 K-D Concentration

The reconcentration of samples is a critical step where serious analyte losses can occur.

Despite the versatility of the K-D evaporative concentrator for solvent reduction in association with a wide variety of organic compounds (e.g. EPA, 1982; Chau and Lee, 1982; Alexander *et al.*, 1983; Standing Committee for Analysts, 1987) and reports of good recoveries (e.g. Junk *et al.*, 1974; Ibrahim *et al.*, 1987; White *et al.*, 1979), it is used less frequently (especially in environmental organic geochemistry) than the rotary evaporation method despite the losses which can occur with the latter method (see Grob and Müller, 1987).

As has been shown by others for other analyses (Chau and Lee, 1982) efficient recovery of added hydrocarbons depends on a number of factors; the solvent, water bath temperature, the final concentration volume required, duration of concentration and the initial concentration of the sample. Table 3.4 shows the time taken to concentrate *n*-pentane, DCM and *n*-hexane to various final concentration volumes. It was found that the temperature had to be at least 14 °C above the boiling point of the solvent tested to achieve concentration in a reasonable time (*ca.* 1 hour). Higher temperatures decrease the time for concentration but also reduce the recovery of standards (Figure 3.5). For example, the concentration of deuterated naphthalene and phenanthrene at 90 °C took only 10 minutes but recoveries were low (40% and 51%, respectively) compared to concentration at 51 °C for 165 minutes (90% and 102%, respectively).

A summary of the results for all recovery tests made using K-D is presented in Table 3.5. The duration of the tests ranged from 22 to 165 minutes with shorter runs failing to provide good recoveries. Overall, the recovery was influenced by the solvent, the original concentration of the solution being concentrated, the water bath temperature and the final concentration volume desired.

Table 3.4 Investigation of water-bath temperature versus time and final concentration volume for different organic solvents (32 mL) using a micro Kuderna-Danish concentrator.

Solvent	B.P of Solvent (°C)	Water Bath Temp. (°C)	Time to Conc. (min)	Final Conc. Volume (mL)
<i>n</i> -Pentane	36.1	46	> 150	NCA
		48	80	1.5
		50	25	1.7
		52	24	0.5
		56	17	1.3
		57	12	1.3
Dichloromethane	39.7	46	> 300	NCA
		51	165	1.0
		56	80	1.0
		66	20	1.0
		90	10	1.0
<i>n</i> -Hexane	69	56	NCA	NCA
		76	NCA	NCA
		84	56	1.8

NCA : No concentration acheived

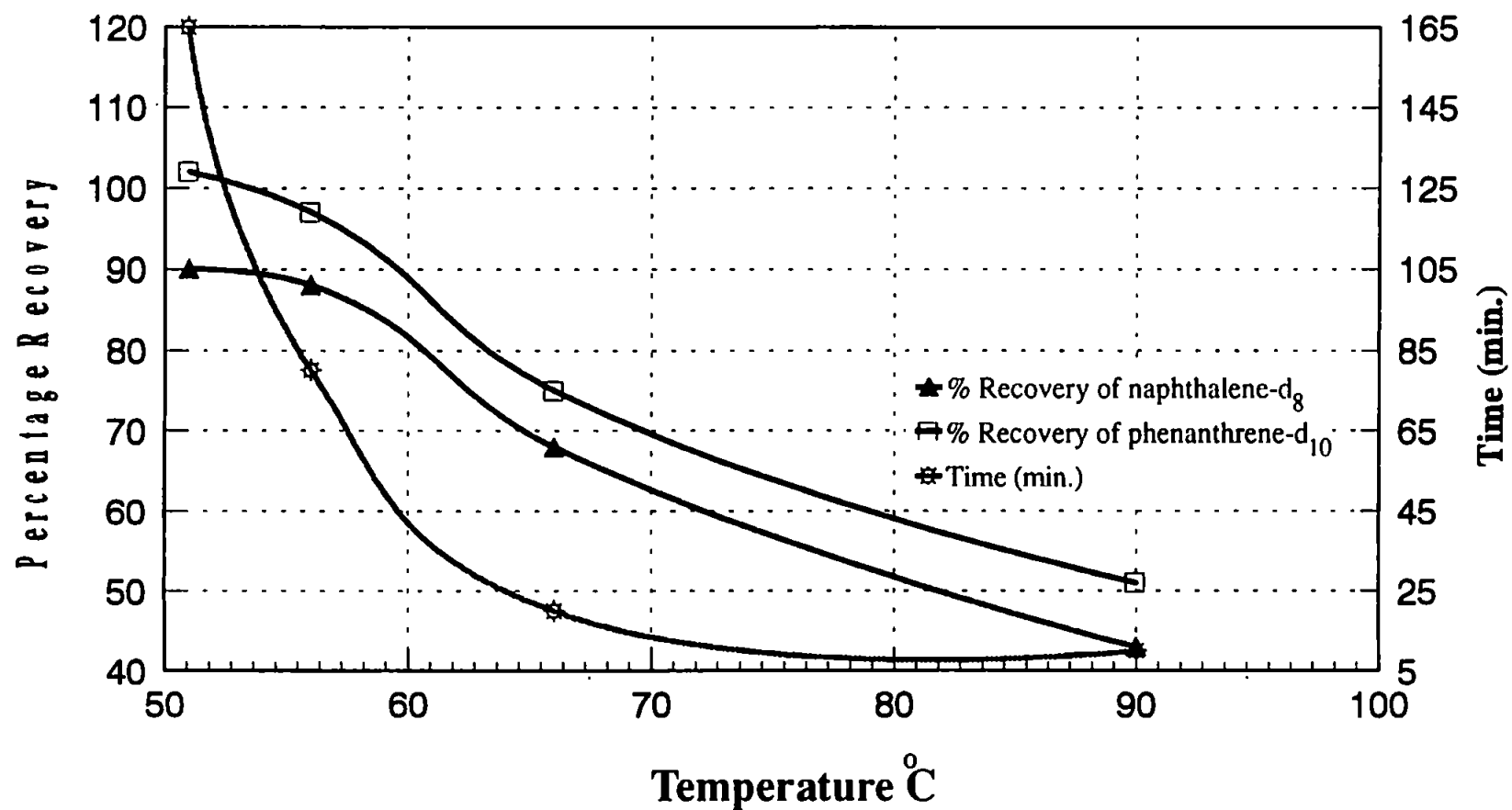


Figure 3.5 Recovery of deuterated naphthalene and phenanthrene standards in DCM versus temperature and time of concentration using a micro Kuderna-Danish concentrator (see Table 3.5).

Table 3.5 Summary of recovery of deuterated hydrocarbons by Kuderna-Danish (K-D) concentrator

Concentrator Type & Size	Solvent	Mixture of Internal Standards Tested & Amount of Each in the Solution	Total Volume for Conc. (ml)	Water Bath Temp. (°C)	Final Conc. Volume (ml)	Duration of Conc. (min.)	Method of Analysis	Average Recovery (%) n=3		
								Benz.-d ₆	Naph.-d ₈	Phen.-d ₁₀
micro K-D 112 mm micro condenser, 40 ml flask and 2 ml receiving vessel with micro connectors or with ground glass joints.	<i>n</i> -Pentane	Benzene-d ₆ , Naphthalene-d ₈ and Phenanthrene-d ₁₀ , 10 µg each	30	50	0.9	46	Cryogenically cooled GC-MS	28	63	65
			31	51	0.65	46		26	63	66
			31	50	0.6	46		21	56	57
	<i>n</i> -Pentane	Benzene-d ₆ , Naphthalene-d ₈ and Phenanthrene-d ₁₀ , 20 µg each	30	50	1.0	40	Cryogenically cooled GC-MS	32	85	86
			30	51	0.7	22		23	79	80
			30	51	0.5	26		22	75	87
	<i>n</i> -Pentane	Naphthalene-d ₈ and Phenanthrene-d ₁₀ , 80 µg each	32	48	1.7	25	GC	—	91	101
			32	48	1.5	25	GC	—	81	95
			32	48	0.8	57	GC	—	76	79
			32	48	0.25	55	GC	—	70	73
	Dichloromethane (DCM)	Naphthalene-d ₈ and Phenanthrene-d ₁₀ , 80 µg each	32	51	1.0	165	GC	—	90	102
			32	56	1.0	80	GC	—	88	97
			32	66	2.0	20	GC	—	68	75
			32	90	2.0	10	GC	—	43	51
	<i>n</i> -Hexane	Naphthalene-d ₈ and Phenanthrene-d ₁₀ , 80 µg each	32	84	1.8	56	GC	—	60	62
macro K-D 310 mm macro Snyder column, 250 ml flask, 10 ml receiving vessel with ground glass joints.	<i>n</i> -Pentane	Benzene-d ₆ , Naphthalene-d ₈ and Phenanthrene-d ₁₀ , 10 µg each	30	53	0.9	135	Cryogenically cooled GC-MS	0	21	49

It was found, in agreement with the findings of Ferreira *et al.* (1993), that the higher the initial concentration of material tested, the higher the recovery. Also, the lower the final concentration volume the lower the recovery. For example, recoveries of > 90% (n=3) were obtained using an initial concentration solution mixture of 80 $\mu\text{g mL}^{-1}$ naphthalene- d_8 and 80 $\mu\text{g mL}^{-1}$ phenanthrene- d_{10} in *n*-pentane in 1.7 mL final concentrate. However, the recovery was reduced to 70% when the final volume of these two compounds was reduced to 0.25 mL. Additionally, in a test using a combined solution of deuterated benzene, naphthalene and phenanthrene at a lower initial concentrations (10 $\mu\text{g mL}^{-1}$ each) the recovery of the more volatile benzene- d_6 was low (28%). The recoveries of the relatively less volatile naphthalene- d_8 and phenanthrene- d_{10} were still > 60% in < 1 mL of final concentrate. Nonetheless these recoveries are much better than those reported for naphthalene and phenanthrene by rotary evaporator at higher concentrations (e.g. Grob and Müller, 1987). These results indicate that for higher aromatics, losses incurred when using a micro K-D evaporative concentrator to remove *n*-pentane or DCM from solution would be minimal as also found by Ibrahim *et al.* (1987).

Among the three solvents studied, evaporation of *n*-hexane resulted in the lowest recoveries. This is mainly due to the higher boiling point of *n*-hexane compared to that of *n*-pentane and DCM. The solutions therefore had to be concentrated at a higher water bath temperature (84 °C) compared to *n*-pentane and DCM (50 °C and 56 °C, respectively). *n*-Pentane and DCM have good extraction efficiencies for many organic compounds of environmental interest (e.g. pesticides, hydrocarbons) and, in agreement with the findings of Constable *et al.* (1984), this would make them desirable solvents for use with K-D concentration. A macro K-D which can handle larger volumes (500-1000 mL) than the micro K-D (up to 50 mL) did not give good recoveries for naphthalene- d_8 or

phenanthrene-d₁₀ (21% and 49% respectively) when 10 µg of each standard was used. Benzene-d₆ was not recovered by macro K-D. The recoveries might improve if higher amounts of standards were used but this was not investigated. Since most of the work done here did not require more than 10-20 mL of solvent for sample extraction, the use of macro K-D was not essential.

The recoveries obtained for *n*-nonane, *n*-decane, *n*-undecane in Brent crude oil and for naphthalene-d₈ and phenanthrene-d₁₀ all mixed in DCM are shown in Table 3.6. The recoveries were all above 90%. The presence of co-solutes in the crude oil (i.e. any or all the compounds in the oil) may have contributed to the overall recoveries of these relatively volatile *n*-alkanes by increasing the total solute concentration as mentioned earlier. A similar outcome was recorded by Ferreira *et al.* (1993) who found an enhancement in recovery after the addition of an extra amount of one of the solutes in a diluted alcohol solution.

3.4.3 Optimizing the Final Concentrate Volume and the Amount of Deuterated Internal Standards

GC or GC-MS is most often used for the subsequent determination of the individual components which are present in the SWSF (Winters *et al.*, 1977; Lockhart *et al.*, 1984; Murray *et al.*, 1984) and thus only part of the concentrated volume can be used for the analysis. In order to increase the amount of solute material introduced into the GC, the optimum volume of SWSF concentrate from which 1 µL is injected was determined.

It was found to be necessary to concentrate SWSF extracts to a small volume (*ca.* 0.3 mL)

Table 3.6 Recovery of deuterated naphthalene, phenanthrene and C₉, C₁₀ and C₁₁ *n*-alkanes in fresh Brent crude oil in 30 mL DCM using a micro Kuderna-Danish concentrator.

Compound	% Recovery ^{a,b}
Naphthalene-d ₈	92
Phenanthrene-d ₁₀	95
C ₉ <i>n</i> -alkane	97
C ₁₀ <i>n</i> -alkane	94
C ₁₁ <i>n</i> -alkane	103

^a Average of triplicate analyses

^b Concentration time, 80 min; water bath temperature, 56 °C; final concentration volume, 1 mL.

using K-D followed by a very gentle blow-down method in order to increase the limit of detection for most of the SWSF compounds. It was also determined that the addition of 50 μg benzene- d_6 , 10 μg naphthalene- d_8 and 5 μg phenanthrene- d_{10} internal standards to a 50 mL SWSF for quantitation was appropriate for samples both before and after photodegradation.

3.4.4 Storage of SWSF Concentrates

Another major problem associated with the quantitative analysis of samples is caused by losses of solutes as a result of either reducing sample extracts to dryness and reconstituting with solvent before analysis or poor storage conditions. These problems were addressed by Bowers *et al.* (1981) and Grob and Müller (1987). Because of the susceptibility of the majority of SWSF to losses through volatilisation, it was necessary to optimise the storage procedure in order to preserve the integrity of the samples after reconcentration until the time of analysis. The results of the investigation using sample volumes < 0.5 mL *n*-pentane stored under different conditions are summarised in Table 3.7.

The worst recoveries were obtained when type 1 screw capped vials with an aluminum foil liner were left on the laboratory bench. Fifty five percent of the solvent was lost after 17 days, with 100% lost after 33 days. The best results with type 1 vials were achieved by storing samples in screw capped vials without an aluminum foil liner in a freezer; losses were only 8.7% after 54 days of storage.

Type 2 vials stored either inside or outside the refrigerator showed 100% losses after 40 days. However, solvent in vials stored in the freezer showed only a 7.5 % loss after 40

Table 3.7 Percentage loss of solvents from vials stored under different conditions.

Vial Type (1) (Screw Top Vial)													
Vial Storage Condition	Day 0	Day 2	Day 3	Day 4	Day 5	Day 7	Day 9	Day 12	Day 17	Day 21	Day 33	Day 40	Day 54
LAB + RT	0	0.8	1.5	1.7	1.9	2.6	2.9	4.5	6.7	8.5	11.5	15.0	25.8
LAB + RT + Al Foil	0	0.61	4.6	8.0	11	11.2	24.4	36.1	54.7	69.5	100	100	100
-20 °C	0	--	--	0.03	0.1	0.5	0.7	2.7	2.7	3.0	3.9	4.5	8.7
-20 °C + Al Foil	0	0.5	1.5	2.9	4.4	5.5	6.8	8.3	12.5	15.0	22.5	26.2	34.6
Vials Type (2) (Septum Seal Vial)													
LAB + RT	0				5		9.3			9.8	9.8	100	
4 °C	0				1.4		4			9.8	10	100	
-20 °C	0				0.5		1.2			3.5	7.5	7.5	

(LAB + RT) = Laboratory stored at room temperature;

(LAB + RT + Al Foil) = Laboratory stored at room temperature with aluminium foil liner;

(-20 °C + Al Foil) = Freezer with aluminium foil liner.

days. Losses of 100% were reported by Bowers *et al.* (1981) for biphenyl and fluorene in a 10 $\mu\text{g mL}^{-1}$ hydrocarbon mixture, and 50% and 30%, respectively at 10 times higher concentrations when vials were left with screw-caps loosely fastened at room temperature.

In conclusion, it was found that screw capped vials without an aluminum foil liner provided the best retention of solvents when stored in a freezer for up to 2 months. Thus this method was used for storing the SWSF concentrates. Covering caps with aluminium foil liners creates uneven surfaces under the vial cap which leads to significance sample losses and should be avoided.

3.4.5 Investigation of Sources of contamination

Sample contamination may be experienced at any step in the preparation procedure and a number of potential sources have been reported (e.g. Denney *et al.*, 1978; Karasek *et al.*, 1981; Biedermann and Grob, 1991). Contamination of samples can often be a problem due to interference with the identification and quantification of peaks of interest especially in chromatographic analysis. The effect is further complicated when the constituents of complex mixtures are present in trace amounts, for example environmental samples including hydrocarbons in marine waters (Karasek *et al.*, 1981).

Examples of chromatograms showing the various sources of tested contaminants are presented in Figure 3.6. The concentration of contaminants varied from source to source, but most eluted from the GC columns between 160 °C and about 280 °C. The most common contaminants were found to be phthalate plasticisers (e.g. peak (a) chromatogram A and B, Figure 3.6). Other contaminants included silicones from the grease used for

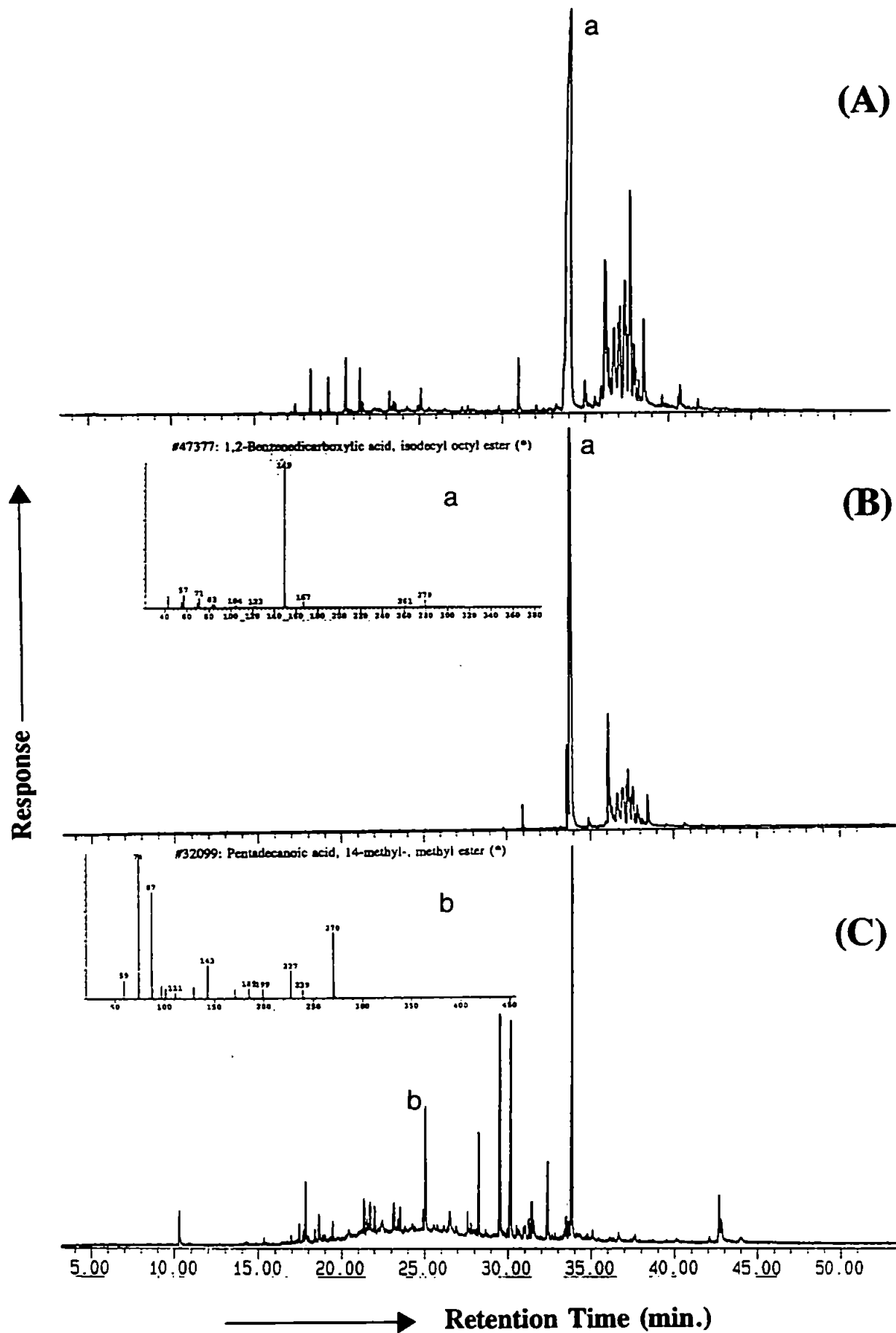


Figure 3.6 Chromatograms showing the various sources of laboratory contamination (A) PTFE tape; (B) pipette fillers; (C) gloves; (D) 'Suba.Seal'; (E) vial septum and (D) silicon grease.

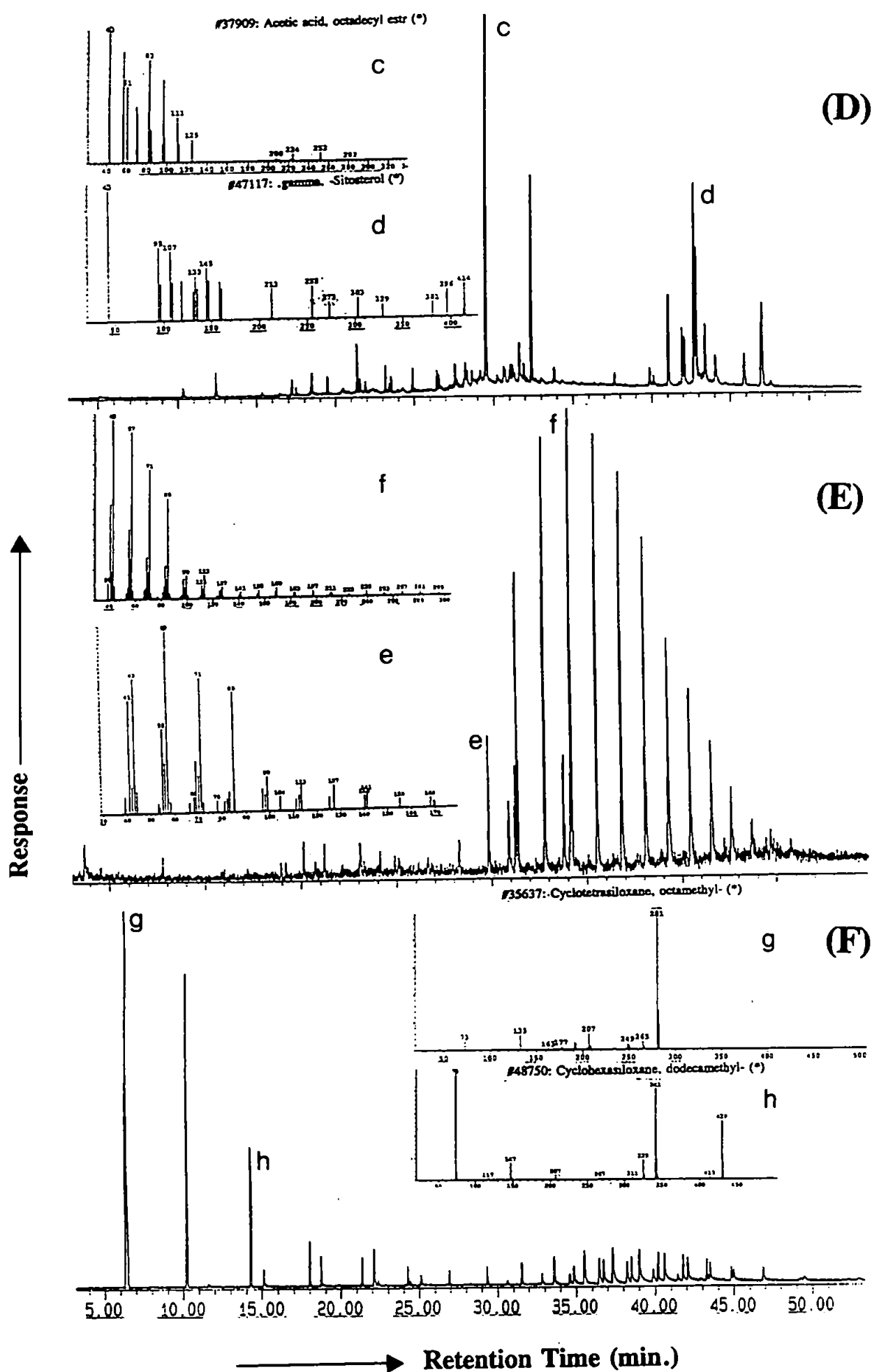


Figure 3.6 "Continued"

lubricating stopcocks in glassware such as in separatory funnels. Contaminants were identified from their mass spectra by comparison with reports in the literature (e.g. Middleditch, 1989) or the GC-MS NBS library spectra. These results could benefit other analysts when facing similar problems.

Residues from contaminants may be left on glassware that has not been thoroughly cleaned using an appropriate method. Consequently, the following procedures were adopted to minimize the possibility of contamination. Although Decon 90 solution is able to emulsify grease and other contaminants, it was found preferable to soak all glassware in a solution of chromic acid for > 48 hr. Each item was then rinsed at least twenty times with distilled water, soaked for 2 hr in deionised water to ensure removal of chromic acid residues and dried at 120 °C overnight. In addition, solvents were checked regularly from their storage flasks and extra care was taken with handling of all glassware and samples.

3.4.6 Characterisation and Quantification of SWSF Compounds by GC-MS

On the basis of the optimisation studies described above, GC-MS was found to provide a reliable method for the determination of the hydrocarbon components which were present in the SWSF samples. Cryogenic cooling was particularly useful for the determination of the most volatile components of the sample. Few previous studies have used cryogenic cooling and measurements of monoaromatic compounds in SWSF solutions have not been always quantitative, with low boiling components frequently not measured.

A typical chromatogram obtained by GC-MS of the SWSF of Kuwait crude oil is shown in **Figure 3.7**. A list of the compounds identified in the SWSF and their retention indices

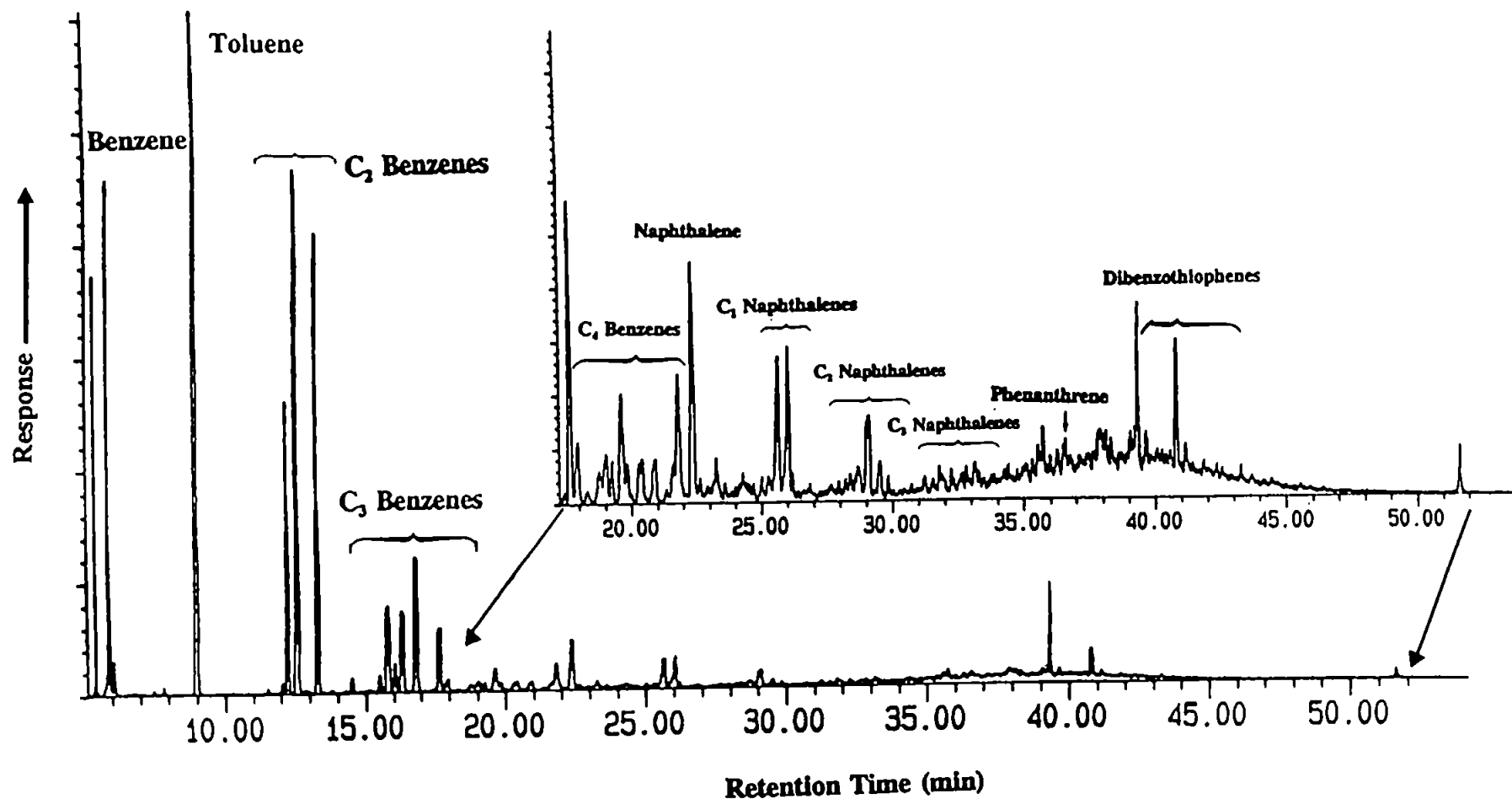


Figure 3.7 Total ion chromatogram of SWSF of fresh unrefined Kuwait crude oil.

(RI) is given in Table 3.8.

The major feature of the chromatogram is a series of resolved low molecular weight aromatic hydrocarbons comprising mainly alkylbenzenes (C_{10-14}) and alkylnaphthalenes (C_{15-20}). Only trace quantities of light saturated hydrocarbons, including *n*-heptane and methylcyclohexane, were observed. This implies the virtual absence of suspended oil droplets which often introduce large amounts of alkanes into the solution (see for example Boylan and Tripp, 1971). Minor compounds such as biphenyl, dibenzothiophene and phenanthrene were also identified from their mass spectra. The observations support previously reported laboratory studies on the dissolution of a variety of crude oils (e.g. Burwood and Speers, 1974; Mackay and Shiu, 1976; Pearson *et al.*, 1980; Shiu *et al.*, 1990) in that a major initial process appears to be the selective dissolution of mainly aromatic hydrocarbon components. However, the GC-MS chromatogram in the present study also showed some complexity after a retention time of 30 minutes indicating the presence of traces of higher molecular mass compounds (> 200 Dalton).

There were only a few peaks which were not related to SWSF which could either have originated from the solvent, seawater or other sources of contamination. The origin of these peaks was identified by comparing their retention times and mass spectra with those obtained from the analysis of solvent blanks (*n*-pentane), seawater blanks or materials which introduced some common contaminants; all prepared for this purpose.

Peaks originating from the solvent appeared before 7 minutes retention time on the TIC of SWSF; methylcyclopentane appeared at 5.4 min; cyclohexane at 6.1 min and 2-methylhexane at 6.6 min. No further components were observed in the remainder of the

Table 3.8 Kovats retention indices of compounds identified in the SWSF of Kuwait crude oil.

No	Compound	Mol. Wt.	RI		Characteristic ions
			Exp.	Literature ^d	
1	Benzene ^b	78	632.8	640.0	77,78
2	Toluene ^b	92	745.5	746.4	91,92
3	Ethylbenzene ^b	106	840.4	841.8	91,105,106
4	1,3-Dimethylbenzene ^b	106	850.2	851.1	91,105,106
5	1,4-Dimethylbenzene ^b	106	850.2	851.3	91,105,106
6	1,2-Dimethylbenzene ^b	106	870.7	871.6	91,105,106
7	Isopropylbenzene ^a	120	904.7	906.2	91,105,120
8	<i>n</i> -Propylbenzene ^a	120	933.9	936.0	91,105,120
9	1-Ethyl-3-methylbenzene ^a	120	941.8	944.0	91,105,120
10	1-Ethyl-4-methylbenzene ^a	120	943.0	945.9	91,105,120
11	1,3,5-Trimethylbenzene ^a	120	949.3	951.8	105,119,120
12	1-Ethyl-2-methylbenzene ^a	120	957.2	960.2	91,105,120
13	1,2,4-Trimethylbenzene ^a	120	972.3	975.5	105,119,120
14	1,2,3-Trimethylbenzene ^a	120	996.7	1000.0	105,119,120
15	<i>sec</i> -Butylbenzene ^a	134	990.1	994.0	91,105,134
16	1-Isopropyl-3-methylbenzene ^a	134	1002.3	1005.6	91,119,134
17	1-Isopropyl-4-methylbenzene ^a	134	1002.9	1008.4	91,119,134
18	1-Isopropyl-2-methylbenzene ^a	134	1017.7	1020.7	91,119,134
19	1,3-Diethylbenzene ^a	134	1029.0	1032.1	105,119,134
20	1-Methyl-3-propylbenzene ^a	134	1030.2	1034.5	105,134
21	1,4-Diethylbenzene ^a	134	1036.0	1038.0	105,119,134
22	1,3-Dimethyl-5-ethylbenzene ^a	134	1073.3	1041.6	119,134
23	1,2-Diethylbenzene ^a	134	1039.6	1042.5	105,119,134
24	1-Methyl-2-propylbenzene ^a	134	1044.4	1048.6	105,134
25	1,4-Dimethyl-2-ethylbenzene ^a	134	1057.3	1059.5	119,134

"continued..."

Table 3.8 "continued"

No	Compound	Mol. Wt.	RI		Characteristic ions
			Exp.	Literature ^d	
26	1,3-Dimethyl-4-ethylbenzene ^a	134	1057.6	1060.7	119,134
27	1,2-Dimethyl-4-ethylbenzene ^a	134	1062.1	1066.7	119,134
28	1,3-Dimethyl-2-ethylbenzene ^a	134	1068.5	1071.7	119,134
29	1,2-Dimethyl-3-ethylbenzene ^a	134	1081.7	1085.2	119,134
30	1,2,4,5-Tetramethylbenzene ^a	134	1094.6	1097.8	119,134
31	1,2,3,5-Tetramethylbenzene ^a	134	1096.8	1100.0	119,134
32	1,2,3,4-Tetramethylbenzene ^a	134	1124.8	1130.4	119,134
33	Naphthalene ^b	128	1145.1	n.d.	128
34	2-Methylnaphthalene ^b	142	1256.3	n.d.	141,142
35	1-Methylnaphthalene ^b	142	1270.2	n.d.	141,142
36	1+2-Ethyl naphthalene ^{b,c}	156	1355.2	n.d.	141,156
37	2,6-Dimethylnaphthalene ^{b,c}	156	1366.1	n.d.	141,156
38	2,7-Dimethylnaphthalene ^{b,c}	156	1366.1	n.d.	141,156
39	1,3-Dimethylnaphthalene ^{b,c}	156	1379.3	n.d.	141,156
40	1,7-Dimethylnaphthalene ^{b,c}	156	1379.3	n.d.	141,156
41	1,6-Dimethylnaphthalene ^{b,c}	156	1382.0	n.d.	141,156
42	2,3-Dimethylnaphthalene ^{b,c}	156	1398.4	n.d.	141,156
43	1,4-Dimethylnaphthalene ^{b,c}	156	1398.4	n.d.	141,156
44	1,5-Dimethylnaphthalene ^{b,c}	156	1398.4	n.d.	141,156
45	1,2-Dimethylnaphthalene ^{b,c}	156	1410.4	n.d.	141,156
46	1,3,7-Trimethylnaphthalene ^{b,c}	170	1484.9	n.d.	155,170
47	1,3,6-Trimethylnaphthalene ^{b,c}	170	1488.6	n.d.	155,170
48	1,3,5-Trimethylnaphthalene ^{b,c}	170	1503.2	n.d.	155,170
49	1,4,6-Trimethylnaphthalene ^{b,c}	170	1503.2	n.d.	155,170

"continued..."

Table 3.8 "continued"

No	Compound	Mol. Wt.	RI		Characteristic ions
			Exp.	Literature ^d	
50	2,3,6-Trimethylnaphthalene ^{b,c}	170	1506.3	n.d.	155,170
51	1,2,7-Trimethylnaphthalene ^{b,c}	170	1519.8	n.d.	155,170
52	1,6,7-Trimethylnaphthalene ^{b,c}	170	1519.8	n.d.	155,170
53	1,2,6-Trimethylnaphthalene ^{b,c}	170	1519.8	n.d.	155,170
54	1,2,4-Trimethylnaphthalene ^{b,c}	170	1532.5	n.d.	155,170
55	1,2,5-Trimethylnaphthalene ^{b,c}	170	1539.6	n.d.	155,170
56	Biphenyl ^b	154	1338.8	n.d.	154
57	Dibenzothiophene ^{b,c}	184	1688.3	n.d.	184
58	Phenanthrene ^a	178	1715.4	n.d.	178

a = Authentic standard, b = Mass spectral evidence, c = Comparison with published GC retention data.

^d Hartgers *et al.* (1992). Analysis (n=4) was made with a fused silica capillary column (25 x 0.32 mm I.D) coated with CP Sil-5 (film thickness 0.45 μ m).

n.d. No data available

solvent blank chromatogram (chromatogram A, Figure 3.8).

The analysis of the seawater blank showed a clear chromatogram except for a few very low intensity peaks additional to the solvent peaks identified above (chromatogram B, Figure 3.8). However, these peaks were not seawater-related but were contaminants. Therefore, no organic compounds from the seawater are expected in the SWSF samples.

Two peaks in the SWSF samples were found to arise from contamination; namely the peak at 39.3 min which had a distinctive m/z 149 ion and was identified as phthalate plasticizer and another peak at retention time 12.0 min with a strong m/z 207 ion identified, by a good library match with hexamethylcyclotrisiloxane, as a silicone contaminant. Column bleed such as that from DB-1 stationary phase can also give rise to m/z 207 (as base peak, along with m/z 281, 43 %) at programme temperatures $> 300\text{ }^{\circ}\text{C}$ (see Peters and Moldowan, 1993).

Identification of SWSF Components

Most of the laboratory studies carried out previously have attempted to characterise SWSF according to classes of compounds such as C_2 , C_3 naphthalenes etc (e.g. Anderson *et al.*, 1974; Pearson *et al.*, 1980; Østgaard *et al.*, 1984) and have provided only limited data on individual isomers within each group. In the present study, more detailed characterisation was obtained of individual isomers of major groups of compounds in the SWSF of Kuwait crude oil using cryogenically cooled GC-MS and by comparison with authentic compounds. All compounds identified are listed in Table 3.8 and structures are shown in Appendix 1.

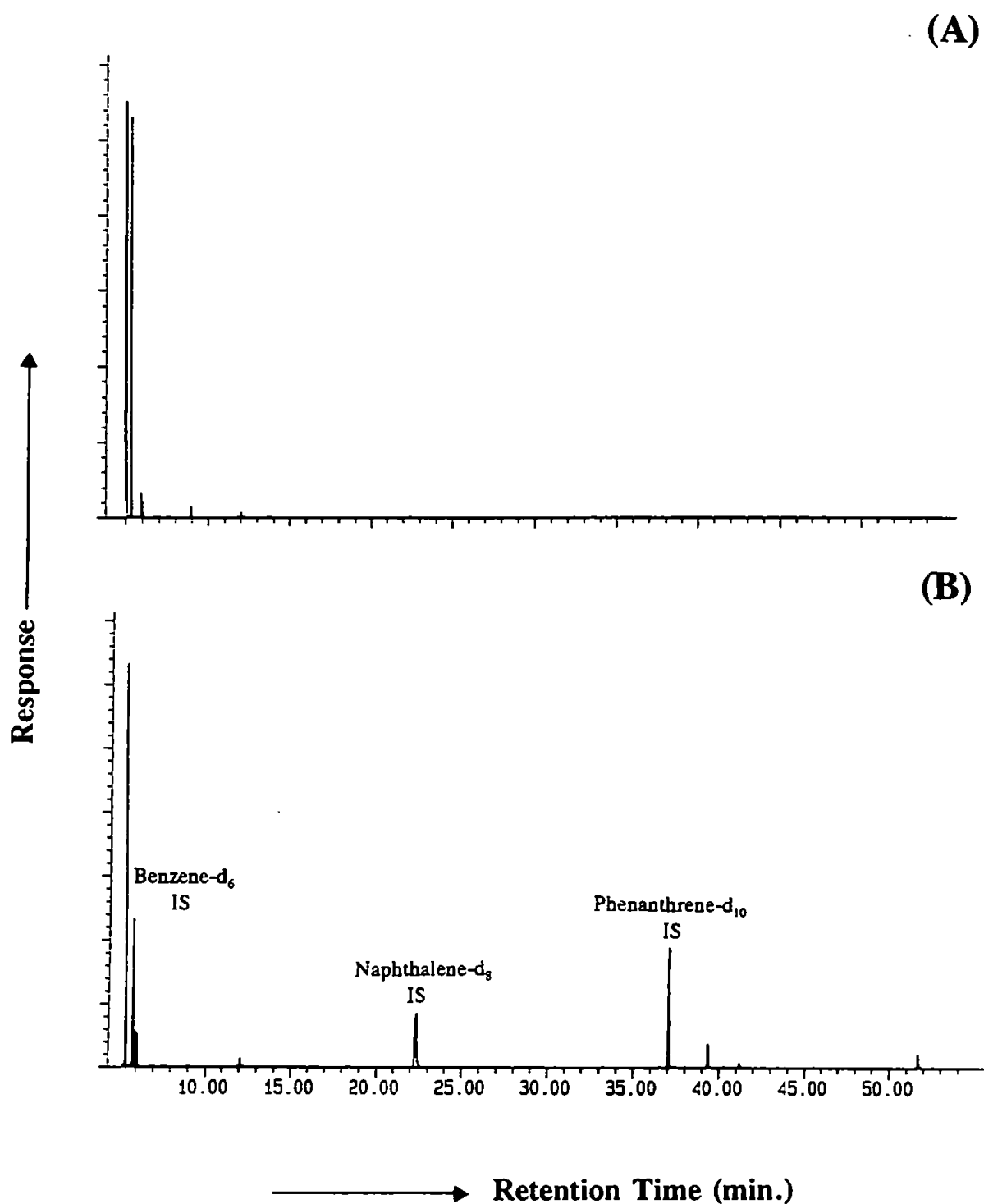


Figure 3.8 Total ion chromatogram of (A) *n*-pentane (100 fold concentration) and (B) *n*-pentane extract of seawater; IS = deuterated internal standards; peaks below 10 minutes are from the solvent; others are contamination by plasticizer and silicon grease.

C₀ and C₁ Substituted Benzene

The abundance of toluene was higher than benzene and indeed it was the most abundant compound in the whole SWSF solution (Figure 3.9). This was also observed in a SWSF of Kuwait crude oil prepared by Anderson *et al.* (1974).

C₂ Substituted Benzenes

The C₂ alkylbenzenes were the second most abundant homologous group in the SWSF (Figure 3.9). Four isomers were identified, 1,3- and 1,4-dimethylbenzene occurred at the same retention time. However, Hartgers *et al.* (1992) found that 1,4-dimethylbenzene was separated by only +0.2 RI unit from the 1,3-dimethylbenzene when analysing the authentic isomers using a CP-Sil 5 phase column (see Table 3.8). The elution order of the dialkylbenzenes was ethylbenzene, 1,3- + 1,4-dimethylbenzenes and finally 1,2-dimethylbenzene (Figure 3.9).

C₃ Substituted Benzenes

Eight isomers were identified. The 1,2,4-trimethylbenzene isomer had the highest abundance (Figure 3.9). Two of the isomers (1-ethyl-3- and 1-ethyl-4-methylbenzene) were only partially resolved, and were regarded as one peak for quantification.

C₄ Substituted Benzenes

C₄ substituted alkylbenzenes were the least abundant benzenes in the SWSF, of which 18 isomers were identified [RI of 22 isomers were reported by Hartgers *et al.* (1992) in kerogen pyrolysates and coal samples]. The isomer which had the highest abundance was the 1,2,3,4-tetramethylbenzene, which was also the last eluting C₄ alkylbenzene isomer in the SWSF. Complete resolution between some of the isomers was not achieved; in these

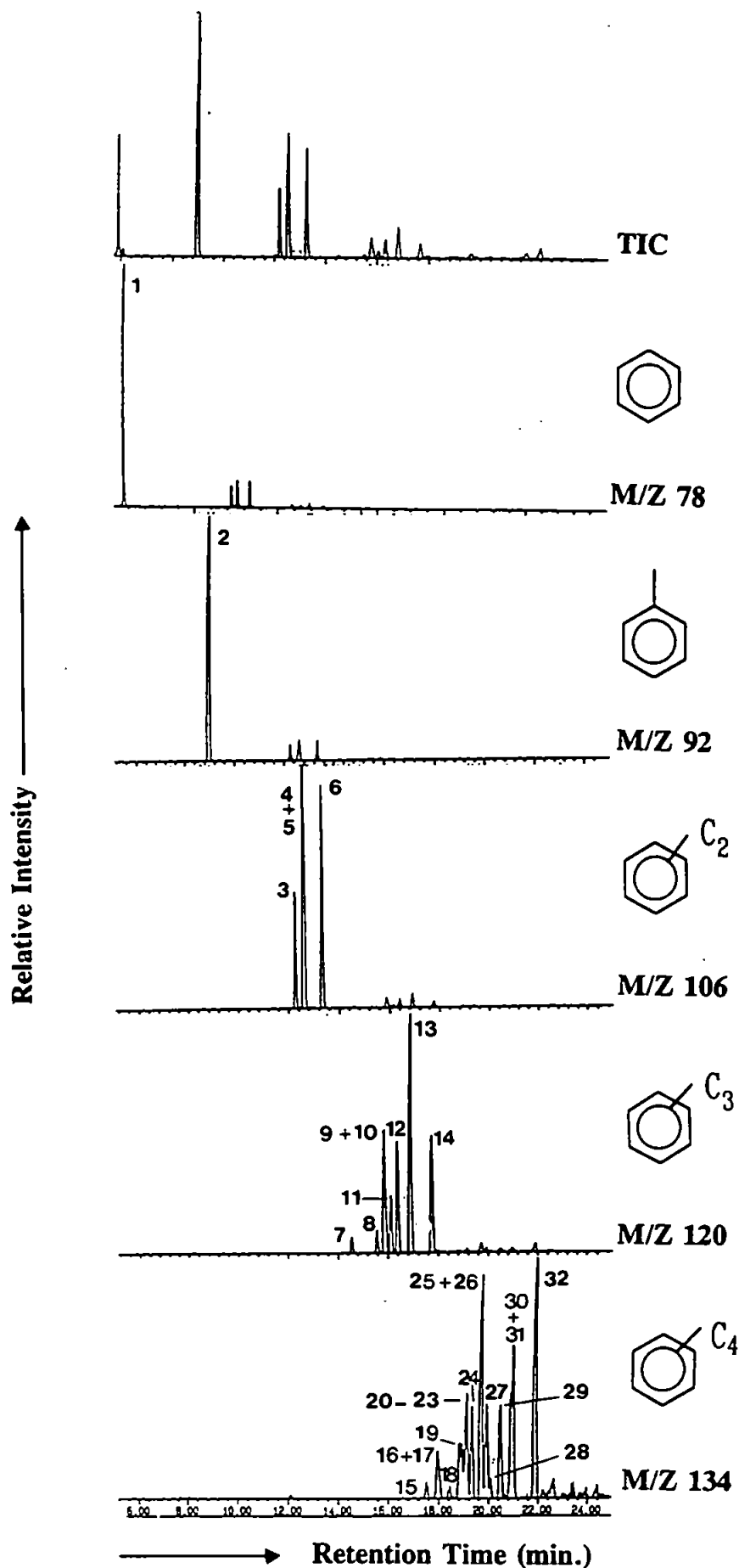


Figure 3.9 Mass chromatograms of SWSF showing the distribution of C_0 - C_4 alkylated benzenes. Peak numbers refer to compounds listed in Table 3.8.

cases, the total area under the co-eluting peak was integrated (Figure 3.9). Comparison of the RI of the identified benzenes with literature values showed good agreement (Table 3.8). Although RI of the SWSF and the authentic compounds were measured from a single run, good agreement with the RI reported by Hartgers *et al.* (1992), which were derived from replicate analyses (n=4), was found. In addition, the reproducibility of the GC-MS was found to be very good ($\pm < 0.1$ RI unit).

Naphthalenes

Naphthalene and its alkylated pseudo homologs were the second most abundant class of compounds in the SWSF. Naphthalene had the highest abundance, followed by the two methyl isomers (Figure 3.10) which were almost equal in intensity to each other. Ten isomers of C₂ alkyl naphthalenes were identified as shown in Figure 3.10. C₃ alkyl naphthalenes (10 isomers) were also identified in the SWSF; however, their abundances were very low (Figure 3.10).

Other Compounds

Minor compounds such as biphenyl, dibenzothiophene and phenanthrene were identified from their mass spectra. No alkylphenanthrenes were found. The composition of the SWSF as reported in this study is in agreement with Anderson *et al.* (1974) who reported the same classes of compounds in a seawater extract prepared from Kuwait crude oil using a slow stirring rate, although only a few isomers were identified within each group.

The presence of alkylated benzothiophene and dibenzothiophenes was indicated by an ion chromatogram which was characteristic for these compounds. For example, use of m/z 162 and 176 showed the presence of C₂ and C₃ alkylbenzothiophenes (Figure 3.11),

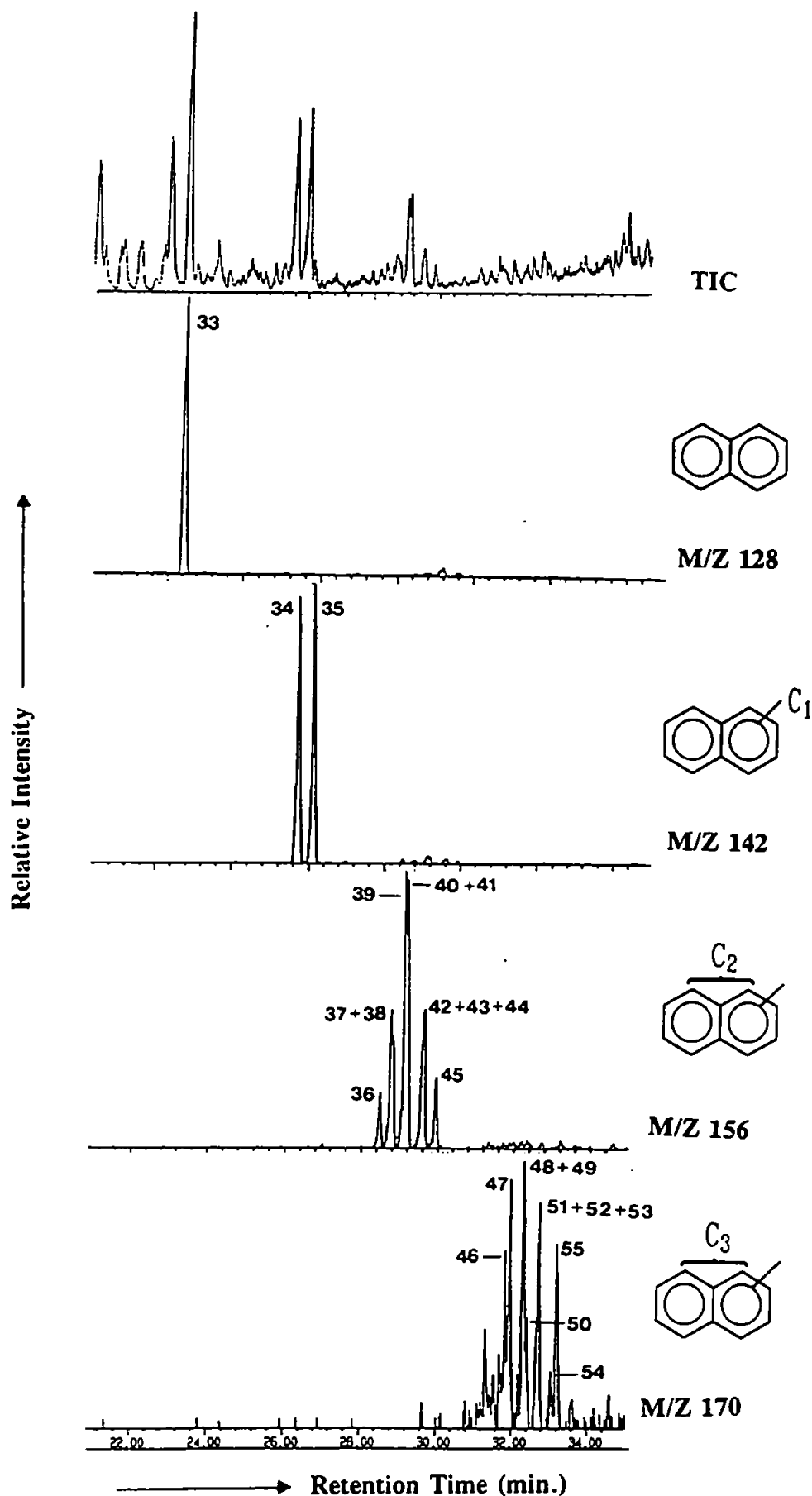
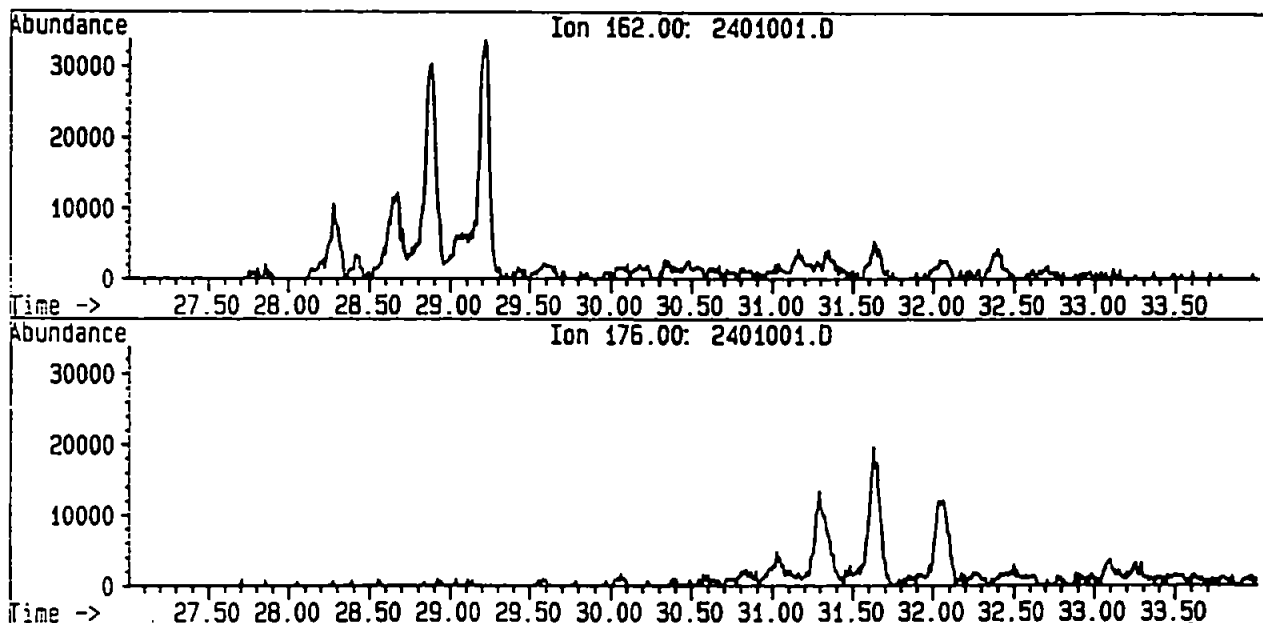


Figure 3.10 Mass chromatograms of SWSF showing the distribution of C₀ - C₃ alkylated naphthalenes. Peak numbers refer to compounds listed in Table 3.8.

File: C:\CHEMPC\DATA\LAWSF4\2401001.D
 Operator: LULWA ALI
 Date Acquired: 24 Nov 92 7:33 pm
 Method File: WSF2.M
 Sample Name: WSF+ n-ALKANE STDS (C9-C25)FOR RI (SCAN)
 Misc Info: SPLITLESS, -20-300 @ 5/min +5, He
 ALS vial: 24

(A)



(B)

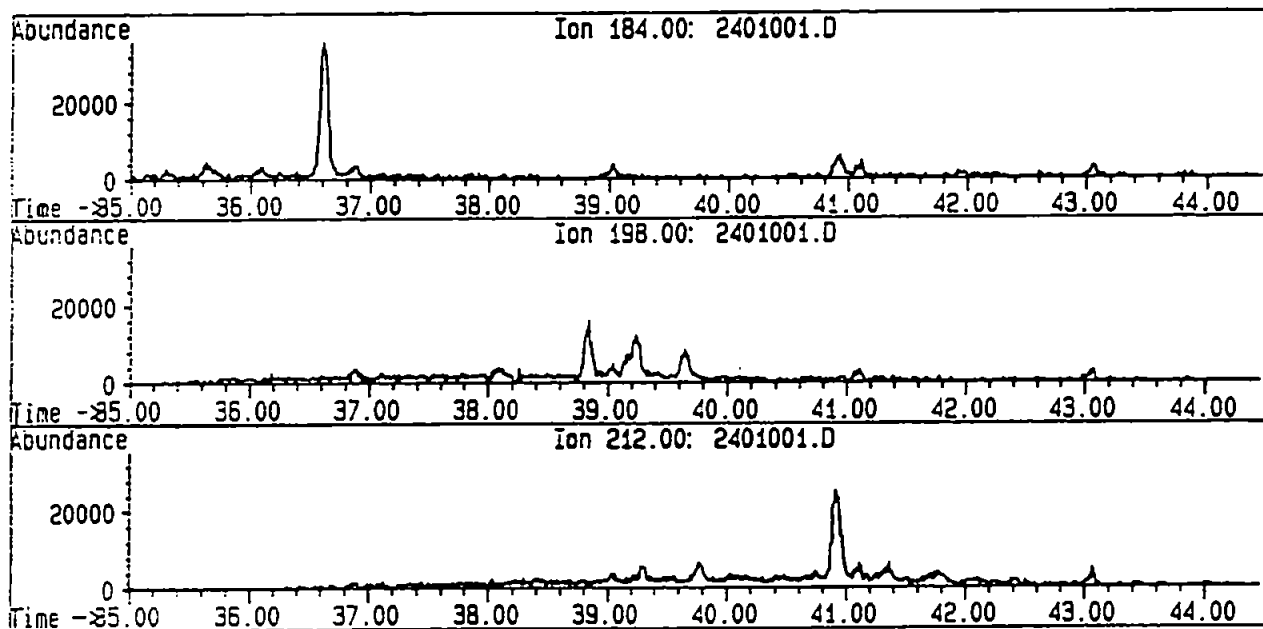


Figure 3.11 Mass chromatograms of SWSF showing the presence of (A) C₂ (m/z 162) and C₃ (m/z 176) alkylated benzothiophenes and (B) C₀ (m/z 184), C₁ (m/z 198) and C₂ (m/z 212) alkylated dibenzothiophenes.

respectively. The ions of 184, 198 and 212 showed the presence of C_{0,2} dibenzothiophenes (Figure 3.11). Positive identification of individual isomers either of these classes of compounds was difficult, partly because they were present in very low amounts and partly because of the complexity of the chromatogram in the region where these compounds appear. Thus, only tentative identifications were made.

The presence of a small amount of a range of C_{2,4} alkyl-substituted phenols was also observed in the region between the methyl- and dimethylnaphthalenes (Figure 3.12). The presence of phenols in SWSF's of crude oils and in crude oils has also been reported by other researchers (e.g. Boylan and Tripp, 1971; Frankenfeld, 1973; Burwood and Speers 1974; Ioppolo *et al.*, 1992; Taylor *et al.*, 1993).

The chemical composition as obtained here for the SWSFs from Kuwait crude oil, is in accordance with previous laboratory studies. Use of gentle stirring techniques with various oils have produced an extract enriched in aromatics, low in alkanes and with a composition very different from the parent oil (e.g. Anderson *et al.*, 1974; Paine *et al.*, 1992). Evidence for the validity of comparing laboratory studies and the natural environment was given by Mackay *et al.* (1981). Filtered seawater collected beneath the Ixtoc I oil platform (Gulf of Mexico) was found to contain an aromatic composition quite similar to that of laboratory-prepared SWSF i.e. more of the soluble alkylbenzenes and naphthalenes as compared to phenanthrenes and dibenzothiophenes.

Quantification of the SWSFs

Estimation of the compounds identified in the SWSF was made possible using GC-MS and the inclusion of deuterated internal standards in the quantification procedure. Use of

File: C:\CHEMPC\DATA\LAWSF4\2401001.D
 Operator: LULWA ALI
 Date Acquired: 24 Nov 92 7:33 pm
 Method File: WSF2.M
 Sample Name: WSF+ n-ALKANE STDS (C9-C25) FOR RI (SCAN)
 Misc Info: SPLITLESS, -20-300 @ 5/min +5, He
 ALS vial: 24

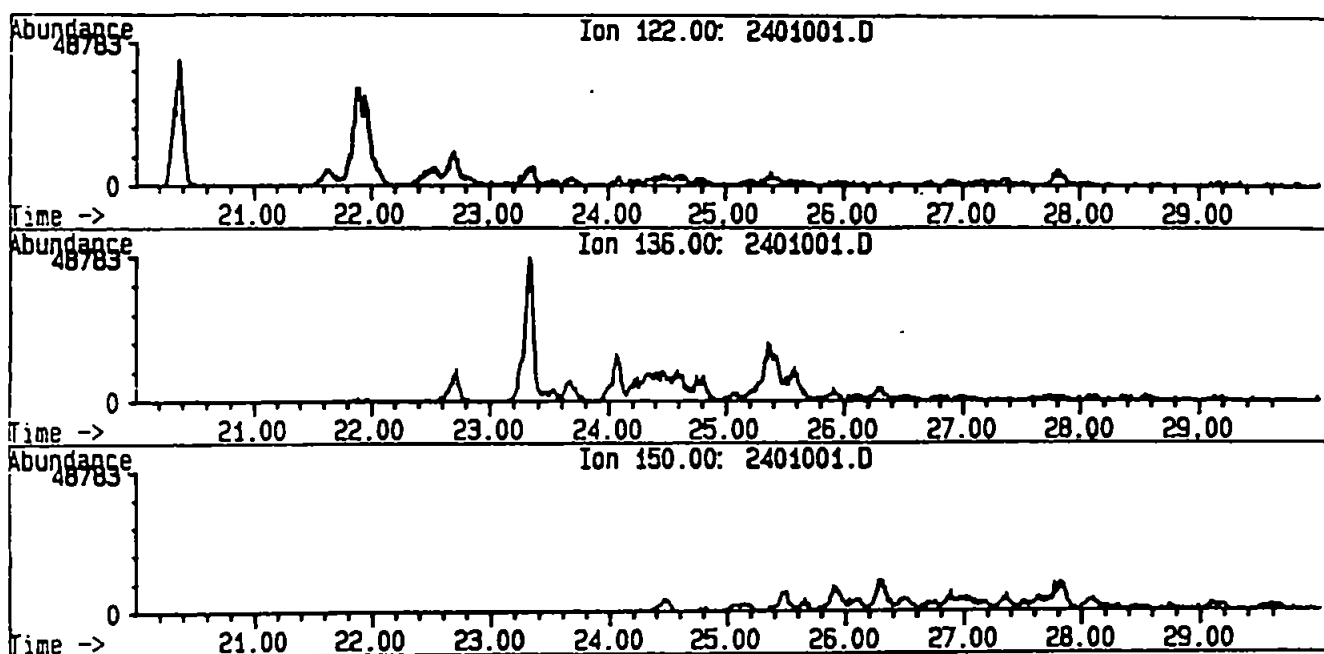


Figure 3.12 Mass chromatograms of SWSF showing the presence of C_2 (m/z 122), C_3 (m/z 136) and C_4 (m/z 150) alkylated phenols.

deuterated internal standards in a relatively complex mixture such as the SWSF is advantageous because the deuterated components have physical and chemical properties that mimic the analytes but have mass spectral features which differentiate them from the non-deuterated analogue and facilitate the quantification of the SWSF peaks.

The recovery of the deuterated internal standards added to the SWSF for the complete workup procedure (extraction, reconcentration with a K-D and N₂ blowdown) were 40%, 80% and 85% for benzene-d₆, naphthalene-d₈ and phenanthrene-d₁₀, respectively. In general, these recoveries are higher than those found in previous studies. The gas chromatographic relative response factors (RF) between the deuterated internal standards and the SWSF compounds were assumed to be equal.

As mentioned in Section 3.3.7, quantification was made by integrating the compound's peak areas, firstly using the molecular ion mass chromatogram (MC) and secondly from the total ion chromatograms (TIC). In both cases comparison was made with peak areas of the molecular ion of the deuterated internal standards.

1- Peaks Integrated from Total Ion Chromatogram (TIC)

The total concentration of the compounds identified as calculated from the TIC was 44.16 µg mL⁻¹ of seawater. A detailed estimation of the various components present in the water extract of Kuwait crude oil is shown in Table 3.9.

Benzenes

The total concentration of all benzene compounds identified was 41.85 µg mL⁻¹ of seawater. Benzene and alkylbenzenes (C₁-C₄) represented 98.2% of the total SWSF

Table 3.9 Concentration of the compounds identified in the SWSF (peaks integrated from total ion chromatogram).

No	Compound *	$\mu\text{g mL}^{-1}$ seawater	% of the total
1	Benzene	1.30	3.11
2	Toluene	13.35	31.91
3	Ethylbenzene	2.84	6.79
4	1,3-Dimethylbenzene +	7.52	17.97
5	1,4-Dimethylbenzene		
6	1,2-Dimethylbenzene	5.41	12.93
7	Isopropylbenzene	0.21	0.50
8	<i>n</i> -Propylbenzene	0.27	0.65
9	1-Ethyl-3-methylbenzene +	1.61	3.85
10	1-Ethyl-4-methylbenzene		
11	1,3,5-Trimethylbenzene	0.49	1.17
12	1-Ethyl-2-methylbenzene	1.32	3.15
13	1,2,4-Trimethylbenzene	2.38	5.69
14	1,2,3-Trimethylbenzene	1.21	2.89
15	<i>sec</i> -Butylbenzene	0.049	0.12
16	1-Isopropyl-3-methylbenzene +	0.34	0.81
17	1-Isopropyl-4-methylbenzene		
18	1-Isopropyl-2-methylbenzene	0.08	0.19
19	1,3-Diethylbenzene	0.20	0.48
20	1-Methyl-3-propylbenzene +	0.32	0.76
21	1,4-Diethylbenzene +		
22	1,3-Dimethyl-5-ethylbenzene +		
23	1,2-Diethylbenzene		
24	1-Methyl-2-propylbenzene	0.18	0.43

"continued..."

Table 3.9 "continued"

No	Compound *	$\mu\text{g mL}^{-1}$ seawater	% of the total
25	1,4-Dimethyl-2-ethylbenzene +	0.63	1.51
26	1,3-Dimethyl-4-ethylbenzene		
27	1,2-Dimethyl-4-ethylbenzene	0.18	0.43
28	1,3-Dimethyl-2-ethylbenzene	0.05	0.12
29	1,2-Dimethyl-3-ethylbenzene	0.19	0.45
30	1,2,4,5-Tetramethylbenzene +	0.27	0.65
31	1,2,3,5-Tetramethylbenzene		
32	1,2,3,4-Tetramethylbenzene	0.71	1.70
33	Naphthalene	0.09	0.22
34	2-Methylnaphthalene	0.13	0.31
35	1-Methylnaphthalene	0.15	0.36
36	1+2-Ethylnaphthalene	0.024	0.06
37	2,6-Dimethylnaphthalene +	0.028	0.07
38	2,7-Dimethylnaphthalene		
39	1,3-Dimethylnaphthalene +	0.059	0.14
40	1,7-Dimethylnaphthalene		
41	1,6-Dimethylnaphthalene	0.043	0.10
42	2,3-Dimethylnaphthalene +	0.042	0.10
43	1,4-Dimethylnaphthalene +		
44	1,5-Dimethylnaphthalene		
45	1,2-Dimethylnaphthalene	0.016	0.04

"continued..."

Table 3.9 "continued"

No	Compound ^a	$\mu\text{g mL}^{-1}$ seawater	% of the total
46	1,3,7-Trimethylnaphthalene	0.02	0.05
47	1,3,6-Trimethylnaphthalene	0.01	0.02
48	1,3,5-Trimethylnaphthalene +	0.02	0.05
49	1,4,6-Trimethylnaphthalene		
50	2,3,6-Trimethylnaphthalene	0.007	0.02
51	1,2,7-Trimethylnaphthalene +	0.02	0.05
52	1,6,7-Trimethylnaphthalene +		
53	1,2,6-Trimethylnaphthalene		
54	1,2,4-Trimethylnaphthalene	0.016	0.04
55	1,2,5-Trimethylnaphthalene	0.013	0.03
56	Biphenyl	0.014	0.03
57	Dibenzothiophene	0.04	0.10
58	Phenanthrene	0.001	0.0002
	Total	41.852	100

^a Isomers which coeluted were integrated as one peak and indicated in the table by the + sign, see also text.

compounds. Toluene was present in the highest concentration in the SWSF at $13.4 \mu\text{g mL}^{-1}$, followed by benzene at $1.3 \mu\text{g mL}^{-1}$ seawater. These two compounds were also found by other researchers to have the highest individual concentration within SWSF produced from various oils (e.g. Mackay and Shiu, 1976; Pearson *et al.*, 1981). The total concentration of C_2 , C_3 and C_4 alkylbenzenes was $15.8 \mu\text{g mL}^{-1}$, $7.5 \mu\text{g mL}^{-1}$ and $3.2 \mu\text{g mL}^{-1}$ seawater, respectively. This makes the C_2 alkylbenzenes the most abundant benzene group in the SWSF.

The higher relative amounts of the benzenes as determined here relative to other components present in the SWSF shows general agreement with other studies on the composition of SWSF. Previous studies have shown that concentrations of monocyclic aromatic hydrocarbons are often high with respect to other components (e.g. Pearson *et al.*, 1980; Murray *et al.*, 1984). Spooners and Corkett (1979) reported $0.78 \mu\text{g mL}^{-1}$ for monocyclic compounds including benzene, toluene and dimethylbenzenes in a SWSF of a Kuwait crude oil stirred at 1:40 oil to seawater ratio for 4 days at 25°C . As seen from the results of this study, using a lower oil to water ratio (i.e. 1:100) benzene, toluene and dimethylbenzenes comprised $27.6 \mu\text{g mL}^{-1}$ in the SWSF of Kuwait crude oil produced after 5 days of slow stirring also at 25°C . This observation supports our contention that benzene and alkylated benzenes contribute significantly to the SWSF of Kuwait crude oil and similar light-medium oils. Hence, if precautions were not taken or if the analytical procedures employed were not adequate then losses of these volatiles could occur thereby resulting in an underestimation of their concentration.

Naphthalenes

Both naphthalene and C_3 alkylnaphthalenes were present at the same concentration of

$\approx 0.1 \mu\text{g mL}^{-1}$ of seawater (Table 3.9). The sum of the concentration of the two methyl isomers was $0.28 \mu\text{g mL}^{-1}$. The total concentration of the ten C_2 alkylnaphthalene isomers was $0.2 \mu\text{g mL}^{-1}$. Thus, the total concentration of naphthalenes ($\text{C}_0\text{-C}_3$) was $0.68 \mu\text{g mL}^{-1}$, which made up 1.62% of the total concentration of the identified SWSF compounds.

Spooner and Corkett (1979) found $0.024 \mu\text{g mL}^{-1}$ of naphthalene, and 0.03 and $0.024 \mu\text{g mL}^{-1}$ of methyl- and dimethylnaphthalene in a SWSF of Kuwait crude oil produced from 1:40 oil to seawater ratio at 25°C . These represent a much lower concentration than those determined in the present study and from a much higher oil to water ratio. The higher concentration obtained from the present study clearly reflects the careful conditions under which these compounds were recovered.

Other Compounds

The total concentration of biphenyl, phenanthrene and dibenzothiophene was $0.06 \mu\text{g mL}^{-1}$ of seawater, which is 0.13% of the total concentration of the identified SWSF compounds (Table 3.9). The low concentration of these components within the SWSF was expected because of their low water solubility and high partition coefficient (more details are provided in Section 3.4.7).

2- Peaks Integrated from Mass Chromatograms (MCs)

The ions used for each class of compound and the concentration of the SWSF is given in Table 3.10. The total concentration of compounds identified was $9.36 \mu\text{g mL}^{-1}$ of seawater.

Table 3.10 Concentration of the compounds identified in the SWSF (peaks integrated from mass chromatograms (MCs)). This can be compared with Table 3.9 where total ion chromatograms (TIC) were used for quantitation.

No.	Compound *	Selected Ion	$\mu\text{g mL}^{-1}$ seawater	% of the total
1	Benzene	78	1.30	13.89
2	Toluene	92	4.34	46.37
3	Ethylbenzene	106	0.28	2.99
4	1,3-Dimethylbenzene +	106	1.19	12.71
5	1,4-Dimethylbenzene	106		
6	1,2-Dimethylbenzene	106	0.82	8.76
7	Isopropylbenzene	120	0.02	0.21
8	<i>n</i> -Propylbenzene	120	0.02	0.21
9	1-Ethyl-3-methylbenzene +	120	0.17	1.82
10	1-Ethyl-4-methylbenzene	120		
11	1,3,5-Trimethylbenzene	120	0.07	0.75
12	1-Ethyl-2-methylbenzene	120	0.14	1.50
13	1,2,4-Trimethylbenzene	120	0.55	5.88
14	1,2,3-Trimethylbenzene	120	0.02	0.21
15	<i>sec</i> -Butylbenzene	134	0.002	0.02
16	1-Isopropyl-3-methylbenzene +	134	0.01	0.11
17	1-Isopropyl-4-methylbenzene	134		
18	1-Isopropyl-2-methylbenzene	134	0.001	0.01
19	1,3-Diethylbenzene	134	0.02	0.21
20	1-Methyl-3-propylbenzene +	134	0.02	0.21
21	1,4-Diethylbenzene +	134		
22	1,3-Dimethyl-5-ethylbenzene +	134		
23	1,2-Diethylbenzene	134		
24	1-Methyl-2-propylbenzene	134	0.02	0.21

"continued..."

Table 3.10 "continued"

No.	Compound *	Selected Ion	$\mu\text{g mL}^{-1}$ seawater	% of the total
25	1,4-Dimethyl-2-ethylbenzene +	134	0.04	0.43
26	1,3-Dimethyl-4-ethylbenzene	134		
27	1,2-Dimethyl-4-ethylbenzene	134	0.02	0.21
28	1,3-Dimethyl-2-ethylbenzene	134	0.004	0.04
29	1,2-Dimethyl-3-ethylbenzene	134	0.02	0.21
30	1,2,4,5-Tetramethylbenzene +	134	0.03	0.32
31	1,2,3,5-Tetramethylbenzene	134		
32	1,2,3,4-Tetramethylbenzene	134	0.05	0.053
33	Naphthalene	128	0.09	0.96
34	2-Methylnaphthalene	142	0.03	0.32
35	1-Methylnaphthalene	142	0.03	0.32
36	1+2-Ethylnaphthalene	156	0.002	0.02
37	2,6-Dimethylnaphthalene +	156	0.01	0.10
38	2,7-Dimethylnaphthalene	156		
39	1,3-Dimethylnaphthalene +	156	0.01	0.10
40	1,7-Dimethylnaphthalene	156		
41	1,6-Dimethylnaphthalene	156	0.01	0.10
42	2,3-Dimethylnaphthalene +	156	0.01	0.10
43	1,4-Dimethylnaphthalene +	156		
44	1,5-Dimethylnaphthalene	156		
45	1,2-Dimethylnaphthalene	156	0.002	0.02

"continued..."

Table 3.10 "continued"

No.	Compound *	Selected Ion	$\mu\text{g mL}^{-1}$ seawater	% of the total
46	1,3,7-Trimethylnaphthalene	170	0.001	0.01
47	1,3,6-Trimethylnaphthalene	170	0.002	0.02
48	1,3,5-Trimethylnaphthalene +	170	0.002	0.02
49	1,4,6-Trimethylnaphthalene	170		
50	2,3,6-Trimethylnaphthalene	170	0.001	0.01
51	1,2,7-Trimethylnaphthalene +	170	0.002	0.02
52	1,6,7-Trimethylnaphthalene +	170		
53	1,2,6-Trimethylnaphthalene	170		
54	1,2,4-Trimethylnaphthalene	170	0.0003	0.003
55	1,2,5-Trimethylnaphthalene	170	0.001	0.01
56	Biphenyl	154	0.002	0.02
57	Dibenzothiophene	184	0.0005	0.005
58	Phenanthrene	178	0.0008	0.008
	Total		9.36	100

* Isomers which coeluted were integrated as one peak and indicated in the table by the + sign, see also text.

Benzenes

The concentration of toluene ($4.3 \mu\text{g mL}^{-1}$) was the highest of all the benzene compounds identified, followed by benzene ($1.3 \mu\text{g mL}^{-1}$). The total concentration of the C_2 alkylbenzenes was $2.3 \mu\text{g mL}^{-1}$, where the 1,3- and 1,4-dimethylbenzene (eluted as one peak) was the highest ($1.2 \mu\text{g mL}^{-1}$). The total concentration of the C_3 alkylbenzenes was $1.0 \mu\text{g mL}^{-1}$, with 1,2,4-trimethylbenzene most abundant ($0.55 \mu\text{g mL}^{-1}$). The total concentration of C_4 alkylbenzenes was $0.24 \mu\text{g mL}^{-1}$ of which 1,2,3,4-tetramethylbenzene had the highest concentration ($0.05 \mu\text{g mL}^{-1}$). The concentration of all benzene compounds (C_{0-4}) was $9.14 \mu\text{g mL}^{-1}$ of seawater, which represented 97.7 % of the total identified SWSF compounds.

Naphthalenes

The concentration of all alkyl naphthalene compounds (C_{0-3}) was $0.2 \mu\text{g mL}^{-1}$ of seawater. The concentration of naphthalene was $0.1 \mu\text{g mL}^{-1}$, the two methyl- isomers had almost the same concentration (total $0.06 \mu\text{g mL}^{-1}$). The total concentration of the C_2 naphthalenes was $0.04 \mu\text{g mL}^{-1}$ and the C_3 naphthalenes was $0.01 \mu\text{g mL}^{-1}$. The concentration of naphthalene compounds (C_{0-3}) was 2.1 % of the total concentration of the identified SWSF compounds.

Other Compounds

The total concentration of biphenyl, dibenzothiophene and phenanthrene was $\approx 0.003 \mu\text{g mL}^{-1}$ of seawater, contributing 0.03% to the total concentration of the identified SWSF compounds.

The type and amount of the soluble fraction of oil that enters the water is very important

since it determines the extent of the toxic effect it may exert on marine life. It has been established that the low molecular weight hydrocarbons constitute the toxic components of oils and particularly benzenes and naphthalenes which are acutely poisonous to humans as well as to marine organisms. These volatile aromatic hydrocarbons are also more water soluble than other constituents and therefore their accurate estimation both as a group and individually is important. The findings of the present study are of particular significance for toxicity studies which often rely on the exposure of different marine species to the SWSF of oil. Data reporting the identity and quantity of toxins may therefore prove very useful. Indeed, Rice *et al.* (1977) have recommended these aspects be incorporated into future toxicity tests. On the other hand, because the low molecular weight components are likely to enter the water column more easily and thus become bioavailable, it is also important to study their photochemical transformations which often generate polar oxygenated and potentially more toxic compounds.

Comparison Between Quantitative Results Obtained by the Two Methods of Integration.

Comparison of the results obtained using TIC and MC integration methods shows that the TIC method yields a much higher concentration ($\approx 41 \mu\text{g mL}^{-1}$) than the MC method ($\approx 9 \mu\text{g mL}^{-1}$). Although neither method is ideal, the MC technique has the advantage of being more selective for the analysis of specific compounds, eliminating interference from other ions (such as those generated from background noise), and, hence, the peak area measured will be lower and could therefore underestimate actual concentrations. In addition, the ion current of the analyte MC plot, relative to its total ion current, will not necessarily be the same as that for the deuterated internal standard. For example, the relative response factor for m/z 142 (C_1 naphthalene) with respect to m/z 136 (naphthalene- d_8) may not be equal to 1. Because of the complex nature of the oil, the MC

method was used for quantifying the individual components in both the oil and the SWSF in order to calculate the partition coefficients.

The TIC, on the other hand, displays the area of all ions associated with the compound and thus the peak area is much higher. However, because the quantification is based on integrating the area of the molecular ion alone for each deuterated internal standard against all the ions for each SWSF compound, this method overestimates the concentration. Integration of full ions of internal standards could not be made because of the co-elution with their corresponding non-deuterated analogues (i.e. benzene, naphthalene and phenanthrene) (see Figure 3.13).

However, the TIC method (which is similar to GC-FID) is particularly useful for integrating peak areas of SWSF samples after photodegradation. The sensitivity is more than that of the mass chromatogram, because the area of total ions of each compound is integrated and, therefore, it enables data (or areas) to be obtained from lower concentrations of SWSF compounds which may occur after a long photodegradation period. Therefore, this method was applied for the quantification of SWSF both before and after photodegradation.

3.4.7 Assessment of the Three Analytical Methods Used for the Quantification of SWSF

The dissolution of petroleum in seawater is a complex process and it depends on chemical, physical and environmental factors as discussed in Chapter 2, Section 2.1. A complete

File: C:\CHEMPC\DATA\LAWSF4\0101001.D
 Operator: LULWA ALI
 Date Acquired: 20 Nov 92 3:50 pm
 Method File: WSF.M
 Sample Name: CONTROL WSF+I.S PENTANE EXTRACT (SCAN)
 Misc Info: SPLITLESS, 12 m HP1, -20 -300 @ 5/min +5, He
 ALS vial: 1

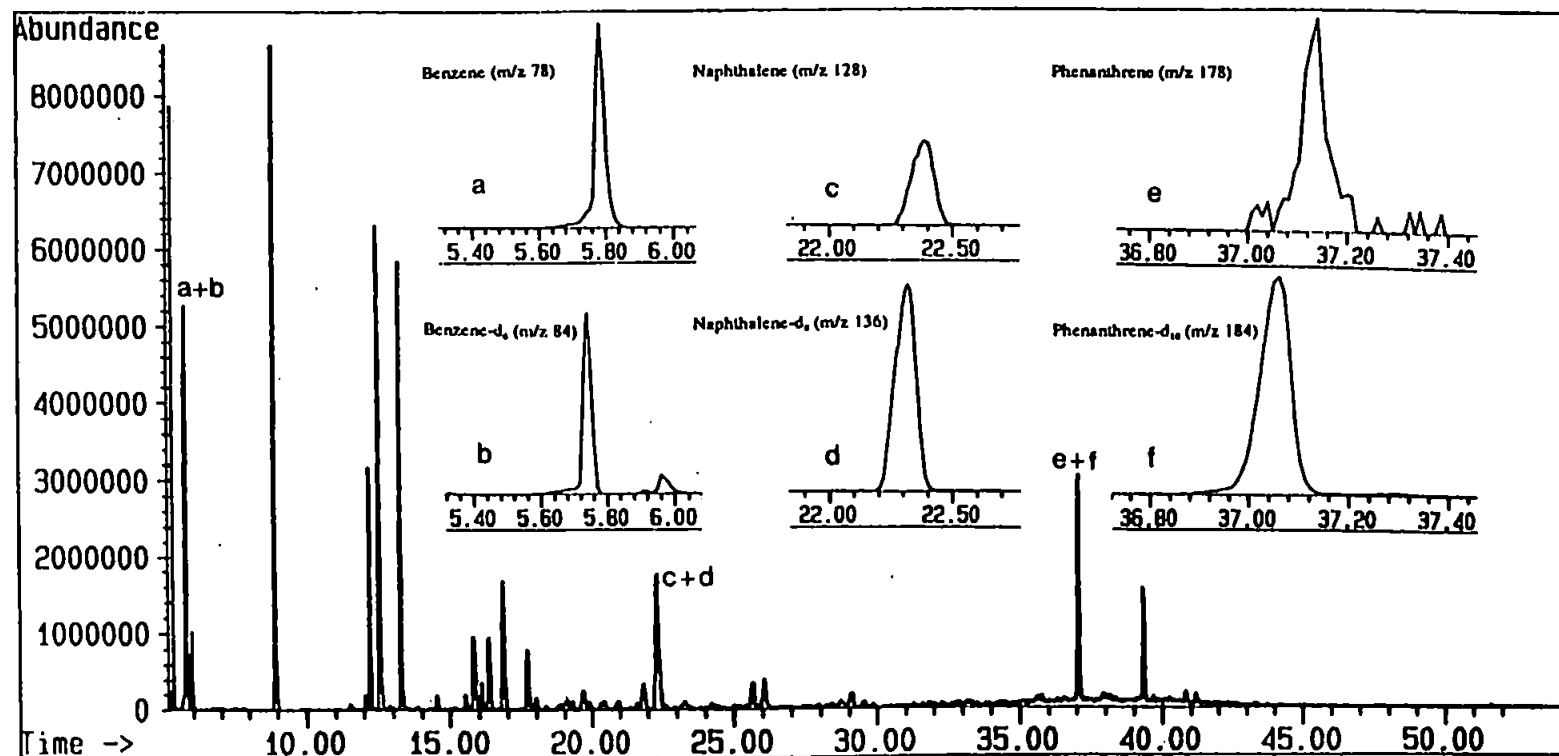


Figure 3.13 TIC chromatogram of SWSF spiked with deuterated internal standards. Inserts show mass chromatograms of the non-deuterated and corresponding deuterated analogues of benzene (a and b), naphthalene (c and d) and phenanthrene (e and f). Note the difference between retention times of the non-deuterated and deuterated compounds.

description of the resulting solution is a complicated analytical problem. Although the analytical methodology is constantly improving, one technique is still insufficient to provide complete details of the content of such a solution (Burns, 1993).

The discussion of the results obtained by UVF (*ca.* 3-4 μg diesel equivalent mL^{-1} seawater), DOC (*ca.* 3-4 μg carbon mL^{-1} seawater) and GC-MS (*ca.* 9 μg weight mL^{-1} seawater from MC and *ca.* 41 μg mL^{-1} from TIC) in this study have to take into account the difference in units and the limitations of the techniques used in each analysis.

In spite of the simplicity, rapidity and sensitivity of UVF, it is at best a semi-quantitative method (Shiu *et al.*, 1990). It is highly dependent on the composition of fluorescent aromatics used in the reference oil (e.g. Law, 1978; Shigehara *et al.*, 1979), and the wavelength at which the analysis is made (Thruston and Knight, 1971; Keizer and Gordon, 1973; Østgaard and Jensen, 1983b; Ehrhardt and Knap, 1989). Aqueous petroleum solutions contain numerous components with individual fluorescent characteristics. For this reason two major difficulties hindered quantification by UVF. It is extremely difficult to find an ideal calibrant which can best represent the petroleum solution mixture, both for direct aqueous sample analysis or the analysis of extracts. Researchers have found that using a solution of the parent crude oil sometime affords the best calibrant (e.g. Law, 1978; Law, 1980). However, since the composition of the aqueous petroleum solution is significantly altered in the marine environment by natural processes (Ehrhardt *et al.*, 1992), it no longer resembles the original oil (see also Section 3.4.7 for a chromatogram of Kuwait crude oil and the SWSF of the oil). Therefore, use of the original oil as a calibrant is inappropriate in such cases. Using diesel oil or other calibrants of more representative composition (e.g. Gordon *et al.*, 1973; Coleman *et al.*, 1984; Hellou and

Pyne, 1987) is then more useful. In addition, because of the individual fluorescence characteristics and excitation optima of each compound in an aqueous petroleum solution, different fluorescence emission spectra are produced for the same sample by a small change in the excitation wavelength. No one set of optimal wavelengths is suitable for all compounds in a petroleum mixture. Thus, the results of quantification would again depend directly on the wavelength used for the analysis. For example, only a small difference in the excitation wavelength between naphthalene and 2,3,5-trimethylnaphthalene exists, but the fluorescence intensity of the latter is more than 10 times that of naphthalene (Østgaard and Jensen, 1983b).

In the present study, the results obtained for the SWSF compounds by direct UVF analysis were based on diesel oil solutions for calibration. These showed good similarity to the fluorescence emission of the SWSF (see Chapter 2 **Figure 2.11**). Because the measurements were made by simultaneous synchronization of the excitation / emission wavelengths, it produced simplified emission spectra with two maxima and eliminated the difficulty of selecting wavelengths during analysis.

However, the concentration obtained for the SWSF was influenced by a number of other factors. UVF is a measure only of the fluorescent content of the solution. Thus, other non-fluorescent compounds (e.g. benzenes), which are the most abundant components of the SWSF were not included. Additionally, polar compounds (e.g. phenols) may also contribute to the measurements (Theobald, 1989). Although UVF measured directly on the aqueous sample is more sensitive than measuring the extracts, the observed concentration could be reduced by quenching due to the presence of chloride and other ions in the seawater.

Despite the attempts to standardize the UVF method (e.g. Law *et al.*, 1988; Standing Committee of Analysts, 1989), different methods are still widely used and therefore a range of results are obtained (e.g. Shigehara *et al.*, 1979; Boehm and Fiest, 1982; Østgaard and Jensen, 1983b). Thus, it should be useful to compare UVF data with an independent method, such as gravimetric determination or DOC measurement of the solute in the aqueous extract, in order to obtain supplementary information.

The concentration of oil in the SWSF was also monitored during dissolution by measurement of the DOC. Very few studies have used more than one analytical method to monitor oil dissolution. However, whilst DOC and UVF measurements are suitable for monitoring dissolution, neither provides an accurate estimate of oil concentration. The DOC method underestimates volatile constituents (which dominate the SWSF as seen from Table 3.9) because of potential losses of these constituents during CO₂ diffusion from acidified seawater or incomplete oxidation to CO₂ (see review by Wangersky, 1993).

Nevertheless, given the dependence of the UVF method on the reference oil and the difficulty of DOC analyses (Suzuki, 1993), the two methods were in broad agreement. Both methods are less specific and much less accurate than GC-MS but are much faster and less costly (Burns, 1993). Because of its selectivity, GC-MS can be used to confirm the presence of specific compounds and also to provide a quantitative estimation of the individual hydrocarbons in the sample when an internal standard is included in the analysis. Additionally, information on the identity and concentration of individual compounds or isomers that GC-MS provides is particularly important in order to obtain rates of photo- or bio- degradation or formation. For example, it was found that the rate of microbial degradation of alkylnaphthalenes is sensitive to the position, number and type

of the substituent and GC-MS can help to provide this information (Ehrhardt and Burns, 1990).

From the discussion it is not surprising therefore, that the three analytical techniques used in the present study (UVF, DOC, GC-MS) yielded different values for the concentration of oil hydrocarbons in the SWSF of Kuwait crude oil. A similar observation was attained by Anderson *et al.* (1974) when IR and GC were employed in the quantification of a Kuwait SWSF. These conclusions agree with those of Anderson *et al.* (1974), in that as long as the limitations of each technique are understood, a reasonable estimation of the concentration of the petroleum hydrocarbons in water could be made with either method, despite the fact that some methods are more accurate than others.

3.4.8 Partition of Hydrocarbons Between the Oil and Seawater

The concentrations of the various compounds quantified in the SWSF (Table 3.9 and 3.10) are in agreement with the findings of McAuliffe (1966) in that, as the molecular weight of a class of hydrocarbons increases, both vapour pressure and solubility decrease by about the same percentage. However, the dissolution of individual components from an oil is controlled by the partition coefficient (oil/water concentration ratios) and the mole fraction of each component in the aqueous and oil phases, and not purely by the solubility of each component (Doerffer, 1992). Oil spilled in offshore waters was found to be out of equilibrium with respect to dissolution of hydrocarbons. For example a concentration of $0.1 \mu\text{g mL}^{-1}$ was reported for dissolved hydrocarbons (Law, 1978; Law *et al.*, 1987) and this is considerably less than values found herein (e.g. $9.4 \mu\text{g mL}^{-1}$, Section 3.4.6). Hence, if an oil spill occurs near the coastline then water may have an opportunity to be

equilibrated with soluble hydrocarbons present in the oil, particularly in intertidal zones.

In an effort to obtain information about the partition coefficient ($K_{oil/sw}$) of SWSF components, a known concentration of the crude oil was prepared and analysed by cryogenically cooled GC-MS under the same conditions used for the SWSF (Section 3.3.14). The recovery of internal standards added to the oil was high; 73% benzene- d_6 , 98% naphthalene- d_8 and 100% for phenanthrene- d_{10} ; this assured good quantitative estimation. The asphaltene content determined by precipitation was 8% of the whole oil.

The gas chromatogram of the whole oil was compared with that obtained for the SWSF (Figure 3.14). Compared to the parent oil, the SWSF was very enriched in low molecular weight aromatic hydrocarbons. These observations support the contention that the chemical composition of crude oil changes considerably following entry into the water column (hence the use of crude oil as a reference in analyses such as UVF to quantify the oil concentration in an aqueous solution is inappropriate as discussed earlier).

The relative concentrations of hydrocarbons in the SWSF, also contrasted markedly with those in the asphaltene-free parent oil, reflecting the different solubilities and partition coefficients in seawater. The concentrations of compounds in the crude oil which were also identified in the SWSF are given in Table 3.11. The total amount measured was $\approx 30 \mu\text{g mg}^{-1}$ oil. Benzene, toluene, ethylbenzene, dimethylbenzenes, 1-ethyl-3-methylbenzene + 1-ethyl-4-methylbenzene and 1,2,4-trimethylbenzene had the highest concentrations, comprising 54.3% of the total. Remaining C_3 alkylbenzenes comprised 9.3% and C_4 alkylbenzenes 17%, with C_{0-3} naphthalenes accounting for a further 18.4%. Other compounds including biphenyl, dibenzothiophene and phenanthrene made up 1.0%.

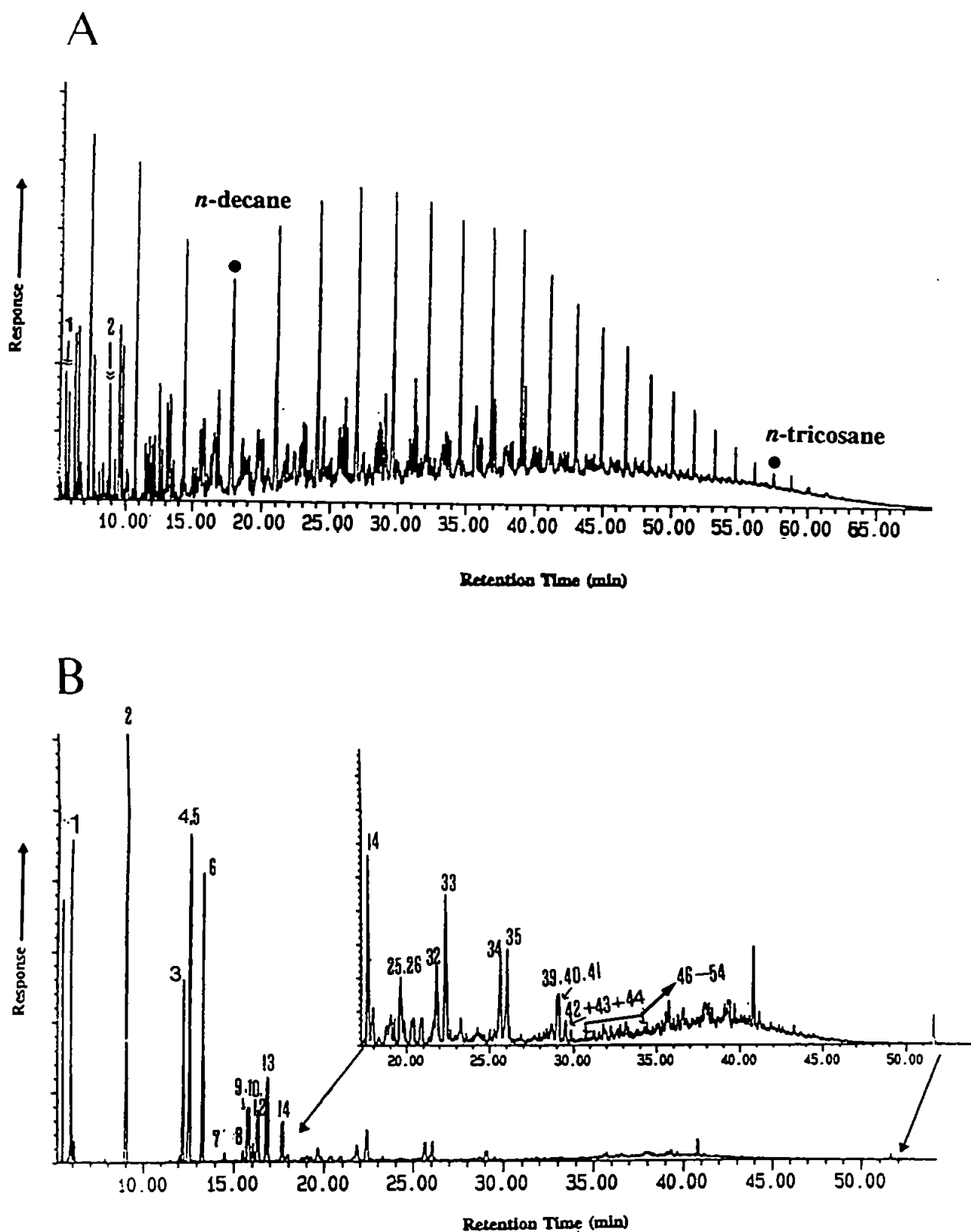


Figure 3.14 Gas chromatograms of (A) fresh unrefined Kuwait crude oil and (B) SWSF prepared from the oil (see text for analysis conditions). Numbers refer to compounds identified in Table 3.11.

Table 3.11 Concentration of the compounds identified in Kuwait crude oil.

No.	Compound *	Selected Ion	$\mu\text{g mg}^{-1}$ oil	% of the total
1	Benzene	78	1.23	4.1
2	Toluene	92	5.74	19.0
3	Ethylbenzene	106	0.96	3.2
4	1,3-Dimethylbenzene +	106	3.12	10.3
5	1,4-Dimethylbenzene	106		
6	1,2-Dimethylbenzene	106	1.52	5.0
7	Isopropylbenzene	120	0.18	0.6
8	<i>n</i> -Propylbenzene	120	0.31	1.0
9	1-Ethyl-3-methylbenzene +	120	1.56	5.2
10	1-Ethyl-4-methylbenzene	120		
11	1,3,5-Trimethylbenzene	120	0.68	2.3
12	1-Ethyl-2-methylbenzene	120	0.87	2.9
13	1,2,4-Trimethylbenzene	120	2.24	7.4
14	1,2,3-Trimethylbenzene	120	0.76	2.5
15	<i>sec</i> -Butylbenzene	134	0.12	0.41
16	1-Isopropyl-3-methylbenzene +	134	0.31	1.0
17	1-Isopropyl-4-methylbenzene	134		
18	1-Isopropyl-2-methylbenzene	134	0.03	0.1
19	1,3-Diethylbenzene	134	0.59	2.0
20	1-Methyl-3-propylbenzene +	134	0.76	2.5
21	1,4-Diethylbenzene +	134		
22	1,3-Dimethyl-5-ethylbenzene +	134		
23	1,2-Diethylbenzene	134		
24	1-Methyl-2-propylbenzene	134	0.43	1.4

"continued..."

Table 3.11 "continued"

No.	Compound ^a	Selected Ion	$\mu\text{g mg}^{-1}$ oil	% of the total
25	1,4-Dimethyl-2-ethylbenzene +	134	0.94	3.1
26	1,3-Dimethyl-4-ethylbenzene	134		
27	1,2-Dimethyl-4-ethylbenzene	134	0.38	1.3
28	1,3-Dimethyl-2-ethylbenzene	134	0.03	0.1
29	1,2-Dimethyl-3-ethylbenzene	134	0.25	0.83
30	1,2,4,5-Tetramethylbenzene +	134	0.65	2.2
31	1,2,3,5-Tetramethylbenzene	134		
32	1,2,3,4-Tetramethylbenzene	134	0.62	2.0
33	Naphthalene	128	0.50	1.6
34	2-Methylnaphthalene	142	0.66	2.2
35	1-Methylnaphthalene	142	0.62	2.0
36	1+2-Ethylnaphthalene	156	0.14	0.47
37	2,6-Dimethylnaphthalene +	156	0.47	1.6
38	2,7-Dimethylnaphthalene	156		
39	1,3-Dimethylnaphthalene +	156	0.58	1.9
40	1,7-Dimethylnaphthalene	156		
41	1,6-Dimethylnaphthalene	156	0.45	1.5
42	2,3-Dimethylnaphthalene +	156	0.36	1.2
43	1,4-Dimethylnaphthalene +	156		
44	1,5-Dimethylnaphthalene	156		
45	1,2-Dimethylnaphthalene	156	0.13	0.44

"continued..."

Table 3.11 "continued"

No.	Compound ^a	Selected Ion	$\mu\text{g mg}^{-1}$ oil	% of the total
46	1,3,7-Trimethylnaphthalene	170	0.21	0.7
47	1,3,6-Trimethylnaphthalene	170	0.38	1.26
48	1,3,5-Trimethylnaphthalene +	170	0.35	1.17
49	1,4,6-Trimethylnaphthalene	170		
50	2,3,6-Trimethylnaphthalene	170	0.14	0.46
51	1,2,7-Trimethylnaphthalene +	170	0.31	1.0
52	1,6,7-Trimethylnaphthalene +	170		
53	1,2,6-Trimethylnaphthalene	170		
54	1,2,4-Trimethylnaphthalene	170	0.06	0.2
55	1,2,5-Trimethylnaphthalene	170	0.21	0.7
56	Biphenyl	154	0.07	0.23
57	Dibenzothiophene	184	0.16	0.53
58	Phenanthrene	178	0.08	0.27
	Total		30.16	100

^a Isomers which coeluted were integrated as one peak and indicated in the table by the sign (+), see also text.

Given a two-phase system consisting of oil (subscript oil), and seawater (sw) of volume v_{oil} and v_{sw} at equilibrium and at the same temperature, then an oil hydrocarbon (such as benzene) will partition between these two phases such that;

$$K_{oil/sw} = (m_{oil}/v_{oil}) / (m_{sw}/v_{sw}) \quad (1)$$

where,

m_{oil} = mass of the hydrocarbon remaining in the oil phase following equilibrium partitioning

v_{oil} = volume of oil phase

m_{sw} = mass of the hydrocarbon accumulating in the water phase following equilibrium partitioning

v_{sw} = volume of seawater phase

If, m_t is the total mass of hydrocarbon in the original oil phase (i.e. before partitioning), it follows that:

$$m_t = m_{oil} + m_{sw}$$

$$m_{oil} = m_t - m_{sw} \quad (2)$$

Substituting equation 2 into equation 1 yields:

$$K_{oil/sw} = \{ (m_t - m_{sw})/v_{oil} \} / (m_{sw}/v_{sw}) \quad (3)$$

Because dissolution was made in an enclosed system (see Chapter 2) the attainment of equilibrium concentrations of SWSF in seawater was assured.

The concentrations determined for the individual components measured in the oil are given in Table 3.10, whereas Table 3.11 details their concentrations in the SWSF. $K_{oil/sw}$ was calculated according to the following example for benzene;

9 mL of Kuwait crude oil (v_{oil}) which is equivalent to 7.9 g Kuwait crude oil (s.g. 0.878 g mL⁻¹) and 850 mL seawater (v_{sw}) was used to produce the SWSF solution. Therefore prior to equilibration total mass of benzene in oil phase of experiment (m_i):

$$= 1.23 * 1000 * 7.9 \mu g$$

$$m_i = 9717 \mu g$$

following the partitioning total mass of benzene in 850 mL SWSF solution (m_{sw}):

$$= 1105 \mu g \text{ (Table 3.12)}$$

Therefore total mass of benzene remaining in oil phase after partitioning (m_{oil}):

$$= 9717 - 1105 = 8612 \mu g \text{ benzene}$$

Therefore from equation 1;

$$\begin{aligned} K_{oil/sw} &= (m_{oil}/v_{oil}) / (m_{sw}/v_{sw}) \\ &= (8612 \mu g \text{ benzene}/9 \text{ mL oil}) / (1105 \mu g \text{ benzene}/850 \text{ mL sw}) \\ &= 736 \end{aligned}$$

This formula was applied to each component and the $K_{oil/sw}$ of all SWSF components calculated (Table 3.12). Oil:water partition coefficients of the major SWSF components increase with increasing alkylation for both benzenes and naphthalenes. $K_{oil/sw}$ for benzenes ranged from 736-52500, whilst for naphthalenes the range was 4831-208125 (Table 3.12).

Table 3.12 Calculation of partition coefficient $K_{oil/sw}$ of the compounds characterised in Kuwait crude oil and in SWSF of the oil as obtained from the dissolution experiment.

No.	Compound	Composition in Oil Phase					Composition in Seawater Phase Following Partitioning			$K_{oil/sw}$
		Prior to Partitioning			Following Partitioning		Conc. in SWSF ($\mu\text{g/mL}$ sw)	Total mass in SWSF solution (μg) (m_{sw}) ^b	m_{sw}/v_{sw} $\mu\text{g/mL}$	
		Conc. in oil ($\mu\text{g/mg}$ oil)	Conc. in oil ($\mu\text{g/g}$ oil)	Total mass in oil phase (μg) (m_o) ^a	Remaining mass in oil phase (μg) (m_o) ^c	m_o/v_o $\mu\text{g/mL}$				
1	Benzene	1.23	1230	9717	8612	957	1.3	1105	1.3	736
2	Toluene	5.74	5740	45346	41691	4632	4.3	3655	4.3	1077
3	Ethylbenzene	0.96	960	7584	7346	816	0.28	238	0.28	2914
4	1,3-Dimethylbenzene +	3.12	3120	24648	23628	2625	1.2	1020	1.2	2188
5	1,4-Dimethylbenzene									
6	1,2-Dimethylbenzene	1.52	1520	12008	11311	1257	0.82	697	0.82	1533
7	Isopropylbenzene	0.18	180	1422	1408	156	0.017	14.5	0.017	9176
8	<i>n</i> -Propylbenzene	0.31	310	2449	2429	270	0.024	20.4	0.024	11250
9	1-Ethyl-3-methylbenzene +	1.56	1560	12324	12180	1353	0.17	144.5	0.17	7959
10	1-Ethyl-4-methylbenzene									
11	1,3,5-Trimethylbenzene	0.68	680	5372	5313	590	0.07	59.5	0.07	8429
12	1-Ethyl-2-methylbenzene	0.87	870	6873	6754	750	0.14	119	0.14	5357
13	1,2,4-Trimethylbenzene	2.24	2240	17696	17229	1914	0.55	467.5	0.55	3480
14	1,2,3-Trimethylbenzene	0.76	760	6004	5990	666	0.016	13.6	0.016	41625
15	<i>sec</i> -Butylbenzene	0.12	120	948	946	105	0.002	1.7	0.002	52500

"Continued..."

Table 3.12 "Continued"

No.	Compound	Composition in Oil Phase					Composition in Seawater Phase Following Partitioning			$K_{oil/sw}$
		Prior to Partitioning			Following Partitioning		Conc. in SWSF ($\mu\text{g/mL sw}$)	Total mass in SWSF solution (μg) (m_{sw}) ^b	m_{sw}/v_{sw} $\mu\text{g/mL}$	
		Conc. in oil ($\mu\text{g/mg oil}$)	Conc. in oil ($\mu\text{g/g oil}$)	Total mass in oil phase (μg) (m_o) ^a	Remaining mass in oil phase μg (m_o) ^c	m_o/v_o $\mu\text{g/mL}$				
16	1-Isopropyl-3-methylbenzene +	0.31	310	2449	2440	271	0.011	9.4	0.011	24636
17	1-Isopropyl-4-methylbenzene									
18	1-Isopropyl-2-methylbenzene	0.03	30	237	236	26	0.001	0.9	0.001	26000
19	1,3-Diethylbenzene	0.59	590	4661	4648	516	0.015	12.8	0.015	34400
20	1-Methyl-3-propylbenzene +	0.76	760	6004	5987	665	0.02	17.0	0.02	33250
21	1,4-Diethylbenzene +									
22	1,3-Dimethyl-5-ethylbenzene +									
23	1,2-Diethylbenzene									
24	1-Methyl-2-propylbenzene	0.43	430	3397	3383	376	0.016	13.6	0.016	23500
25	1,4-Dimethyl-2-ethylbenzene +	0.94	940	7426	7391	821	0.041	34.9	0.041	20024
26	1,3-Dimethyl-4-ethylbenzene									
27	1,2-Dimethyl-4-ethylbenzene	0.38	380	3002	2988	332	0.017	14.5	0.017	19529
28	1,3-Dimethyl-2-ethylbenzene	0.25	250	1975	1961	218	0.017	14.5	0.017	12824
29	1,2-Dimethyl-3-ethylbenzene	0.03	30	237	234	26	0.004	3.4	0.004	6500
30	1,2,4,5-Tetramethylbenzene +	0.65	650	5135	5105	567	0.035	29.8	0.035	16200
31	1,2,3,5-Tetramethylbenzene									

"Continued..."

Table 3.12 "Continued"

No.	Compound	Composition in Oil Phase					Composition in Seawater Phase Following Partitioning			$K_{oll/ow}$
		Prior to Partitioning			Following Partitioning		Conc. in SWSF ($\mu\text{g/mL}$)	Total mass in SWSF solution (μg) (m_{sw}) ^b	m_{sw}/v_{sw} $\mu\text{g/mL}$	
		Conc. in oil ($\mu\text{g/mg oil}$)	Conc. in oil ($\mu\text{g/g oil}$)	Total mass in oil phase (μg) (m_o) ^a	Remaining mass in oil phase (μg) (m_o) ^c	m_o/v_o $\mu\text{g/mL}$				
32	1,2,3,4-Tetramethylbenzene	0.62	620	4898	4853	539	0.053	45.1	0.053	10170
33	Naphthalene	0.5	500	3950	3874	430	0.089	75.7	0.089	4831
34	2-Methylnaphthalene	0.66	660	5214	5189	577	0.029	24.7	0.029	19897
35	1-Methylnaphthalene	0.62	620	4898	4872	541	0.031	26.4	0.031	17452
36	1 + 2-Ethylnaphthalene	0.14	140	1106	1104	123	0.002	1.7	0.002	61500
37	2,6-Dimethylnaphthalene +	0.47	470	3713	3709	412	0.005	4.3	0.005	82400
38	2,7-Dimethylnaphthalene									
39	1,3-Dimethylnaphthalene +	0.58	580	4582	4574	508	0.01	8.5	0.01	50800
40	1,7-Dimethylnaphthalene									
41	1,6-Dimethylnaphthalene	0.45	450	3555	3551	395	0.005	4.3	0.005	79000
42	2,3-Dimethylnaphthalene +	0.36	360	2844	2839	315	0.006	5.1	0.006	52500
43	1,4-Dimethylnaphthalene +									
44	1,5-Dimethylnaphthalene									
45	1,2-Dimethylnaphthalene	0.13	130	1027	1025	114	0.002	1.7	0.002	57000
46	1,3,7-Trimethylnaphthalene	0.21	210	1659	1658	184	0.001	0.9	0.001	184000

"Continued..."

Table 3.12 "Continued"

No.	Compound	Composition in Oil Phase					Composition in Seawater Phase Following Partitioning			K _{oil/sew}
		Prior to Partitioning			Following Partitioning		Conc. in SWSF (μg/mL)	Total mass in SWSF solution (μg) (m _{sw}) ^b	m _{sw} /v _{sw} μg/mL	
		Conc. in oil (μg/mg oil)	Conc. in oil (μg/g oil)	Total mass in oil phase (μg) (m _o) ^a	Remaining mass in Oil Phase μg (m _o) ^c	m _o /v _o μg/mL				
47	1,3,6-Trimethylnaphthalene	0.38	380	3002	3001	333	0.0016	1.4	0.0016	208125
48	1,3,5-Trimethylnaphthalene +	0.35	350	2765	2765	307	0.0018	1.5	0.0018	170556
49	1,4,6-Trimethylnaphthalene									
50	2,3,6-Trimethylnaphthalene	0.14	140	1106	1106	123	0.001	0.9	0.001	123000
51	1,2,7-Trimethylnaphthalene +	0.31	310	2449	2449	272	0.0016	1.4	0.0016	17000
52	1,6,7-Trimethylnaphthalene +									
53	1,2,6-Trimethylnaphthalene									
54	1,2,4-Trimethylnaphthalene	0.06	60	474	474	53	0.0003	0.3	0.0003	176667
55	1,2,5-Trimethylnaphthalene	0.21	210	1659	1659	184	0.0013	1.1	0.0013	141538
56	Biphenyl	0.07	70	553	553	61	0.0025	2.1	0.0025	24400
57	Dibenzothiophene	0.16	160	1264	1264	140	0.0005	0.4	0.0005	280000
58	Phenanthrene	0.08	80	632	632	70	0.0008	0.7	0.0008	87500

^a Volume of oil (v_o) used in the dissolution experiment was 9 mL which is equivalent to 7.9 g based on the crude oil specific gravity (0.878 g/mL)

^b Volume of seawater (v_{sw}) used in the dissolution experiment was 850 mL.

^c $m_o = m_i - m_{sw}$ (see also text)

The environmental impact of an oil spill is determined in part by the concentration of toxic materials in the oil as mentioned previously (Section 3.4.6) and by the extent to which these toxicants partition between oil and water. The ability to measure the mechanism at which toxic constituents of oil partition from the floating oil slick to the underlying water is therefore helpful in understanding the potential environmental effects of oil spills. The calculation of $K_{oil/sw}$ (Table 3.12) confirmed that under the experimental conditions used here, hydrocarbons of high aqueous solubility, such as benzene, toluene and dimethylbenzenes, tended to partition into the aqueous phase to a larger extent than hydrocarbons with low solubilities, such as C_3 alkyl naphthalenes, which remain largely in the oil phase. Components with low partition coefficients, such as the monoaromatics, may therefore be in more direct contact with organisms in the water phase than those with higher partition coefficients such as the triaromatics.

Quantitatively, the most abundant group determined in the SWSF was the benzenes (C_{0-4}) which comprised 98% by weight of total dissolved oil; benzene and toluene alone contributed 60%. However, this group was 74% by weight in the quantified crude oil (see Table 3.11) and benzene and toluene comprised only 23%. On the other hand, naphthalenes (C_{0-3}), the second abundant group in the SWSF, comprised 2.1% of total dissolved oil, and 18% by weight in the quantified crude oil. By using the data obtained in Table 3.12, the following relationship was used to calculate the percentage of individual hydrocarbons dissolved in seawater with respect to their total mass in the oil used initially in the preparation of SWSFs:

% of hydrocarbon (x) in seawater

$$\begin{aligned} &= \{ m_{sw,x} / (m_{sw,x} + m_{oil,x}) \} * 100 \quad (4) \\ &= \{ m_{sw,x} / m_{t,x} \} * 100 \end{aligned}$$

where,

$m_{sw,x}$ = mass of hydrocarbon (x) in seawater

$m_{oil,x}$ = mass of hydrocarbon (x) remaining in oil phase after equilibration

$m_{t,x}$ = total mass of hydrocarbon (x) in oil phase prior to equilibration.

Taking benzene once again as an example it follows that since:

m_{sw} of benzene = 1105 μ g benzene in seawater phase after equilibration

m_t of benzene = 9717 μ g benzene in oil layer prior to equilibration

Therefore,

% of benzene in seawater from the initial oil phase

$$= (1105 / 9717) * 100 = 11.4 \%$$

and % of benzene remaining in the oil phase = 88.6 %

This formula was applied to each compound quantified in the SWSF and results are tabulated in Table 3.13. This is a useful alternative way of viewing the partitioning behaviour/solubility behaviour of each compound. As expected from $K_{oil/sw}$ benzene and toluene had the highest percentages in seawater (11.4 % and 12.4 %, respectively) and concurrently the lowest percentages in the oil phase. The percentages reduced from benzene to the naphthalenes where trimethylnaphthalenes exhibited the minimum percentages in the seawater (< 0.1 %) and almost all remained in the oil phase. The

Table 3.13 Percentage of individual hydrocarbon dissolved in the seawater following partitioning with respect to its total mass in the initial oil used for the preparation of SWSF solution.

No.	Compound	Total mass in initial oil phase (μg) (m_i) ^a	Total mass in SWSF solution (μg) (m_w) ^b	% dissolved in seawater ^c	% remaining in oil phase
1	Benzene	9717	1105	11.4	88.6
2	Toluene	45346	3655	12.4	87.6
3	Ethylbenzene	7584	238	3.1	96.9
4	1,3-Dimethylbenzene +	24648	1020	4.1	95.9
5	1,4-Dimethylbenzene				
6	1,2-Dimethylbenzene	12008	697	5.8	94.2
7	Isopropylbenzene	1422	14.5	1.0	99.0
8	<i>n</i> -Propylbenzene	2449	20.4	0.83	99.2
9	1-Ethyl-3-methylbenzene +	12324	144.5	1.17	98.8
10	1-Ethyl-4-methylbenzene				
11	1,3,5-Trimethylbenzene	5372	59.5	1.11	98.9
12	1-Ethyl-2-methylbenzene	6873	119	1.73	98.3
13	1,2,4-Trimethylbenzene	17696	467.5	2.64	97.4
14	1,2,3-Trimethylbenzene	6004	13.6	0.23	99.8
15	<i>sec</i> -Butylbenzene	948	1.7	0.18	99.8
16	1-Isopropyl-3-methylbenzene +	2449	9.4	0.38	99.6
17	1-Isopropyl-4-methylbenzene				
18	1-Isopropyl-2-methylbenzene	237	0.9	0.38	99.6
19	1,3-Diethylbenzene	4661	12.8	0.27	99.7
20	1-Methyl-3-propylbenzene +	6004	17.0	0.28	99.7
21	1,4-Diethylbenzene +				
22	1,3-Dimethyl-5-ethylbenzene +				
23	1,2-Diethylbenzene				
24	1-Methyl-2-propylbenzene	3397	13.6	0.40	99.6
25	1,4-Dimethyl-2-ethylbenzene +	7426	34.9	0.47	99.5
26	1,3-Dimethyl-4-ethylbenzene				
27	1,2-Dimethyl-4-ethylbenzene	3002	14.5	0.48	99.5
28	1,3-Dimethyl-2-ethylbenzene	1975	14.5	0.73	99.3
29	1,2-Dimethyl-3-ethylbenzene	237	3.4	1.4	98.6

"Continued..."

Table 3.13 "Continued"

No.	Compound	Total mass in initial oil phase (μg) (m_i) ^a	Total mass in SWSF solution (μg) (m_{sw}) ^b	% dissolved in seawater	% remaining in oil phase
30	1,2,4,5-Tetramethylbenzene +	5135	29.8	0.58	99.4
31	1,2,3,5-Tetramethylbenzene				
32	1,2,3,4-Tetramethylbenzene	4898	45.1	0.92	99.0
33	Naphthalene	3950	75.7	1.92	98.1
34	2-Methylnaphthalene	5214	24.7	0.47	99.5
35	1-Methylnaphthalene	4898	26.4	0.54	99.5
36	1+2-Ethylnaphthalene	1106	1.7	0.15	99.9
37	2,6-Dimethylnaphthalene +	3713	4.3	0.11	99.9
38	2,7-Dimethylnaphthalene				
39	1,3-Dimethylnaphthalene +	4582	8.5	0.19	99.8
40	1,7-Dimethylnaphthalene				
41	1,6-Dimethylnaphthalene	3555	4.3	0.12	99.9
42	2,3-Dimethylnaphthalene +	2844	5.1	0.18	99.8
43	1,4-Dimethylnaphthalene +				
44	1,5-Dimethylnaphthalene				
45	1,2-Dimethylnaphthalene	1027	1.7	0.17	99.8
46	1,3,7-Trimethylnaphthalene	1659	0.9	0.05	99.95
47	1,3,6-Trimethylnaphthalene	3002	1.4	0.05	99.95
48	1,3,5-Trimethylnaphthalene +	2765	1.5	0.05	99.95
49	1,4,6-Trimethylnaphthalene				
50	2,3,6-Trimethylnaphthalene	1106	0.9	0.08	99.92
51	1,2,7-Trimethylnaphthalene +	2449	1.4	0.06	99.94
52	1,6,7-Trimethylnaphthalene +				
53	1,2,6-Trimethylnaphthalene				
54	1,2,4-Trimethylnaphthalene	474	0.3	0.06	99.94
55	1,2,5-Trimethylnaphthalene	1659	1.1	0.07	99.93
56	Biphenyl	553	2.1	0.38	99.62
57	Dibenzothiophene	1264	0.4	0.03	99.97
58	Phenanthrene	632	0.7	0.11	99.89

^a and ^b see Table 3.12^c % of hydrocarbon (x) in seawater = $m_{sw,x} / m_{i,x} \cdot 100$ (see also text)

differing percentages possessed by isomers of the same alkyl group are also indicated. This clearly indicates that dissolution is a result of the propensity of the hydrocarbon to partition from the bulk oil to the oil-water interface and decreases with increasing hydrophobicity of the compound.

Correlation Between $\log K_{oil/sw}$ and $\log K_{o/w}$

The partition coefficient of compounds in solvent-water systems often follows log-log relationships (see Schwarzenbach *et al.*, 1993). $\log K_{oil/sw}$ was thus plotted in **Figure 3.15** against literature values of the log octanol-water partition coefficient ($\log K_{o/w}$, **Table 3.14**). Whilst some values of $\log K_{oil/sw}$ were slightly greater than $\log K_{o/w}$ (e.g. C_2 alkylbenzenes) a very good linear correlation between the two was demonstrated (slope (m) = 1.00, $r = 0.9576$, $p < 0.01$). While caution should always be applied to consideration of log/log plots, since small variations in log values are often quite large numbers, this is nonetheless an impressive trend.

The equation of the regression line obtained from the correlation between $\log K_{oil/sw}$ and $\log K_{o/w}$ (**Figure 3.15**) may be expressed as;

$$\log K_{oil/sw} = m \log K_{o/w} + c \quad (5)$$

where,

m is the slope of the regression line = 1.00

c is the intercept constant of the line with Y axis = 0.28

with $m = 1.00$

$$\log K_{oil/sw} = \log K_{o/w} + c$$

$$c = \log K_{oil/sw} - \log K_{o/w} = \log (K_{oil/sw} / K_{o/w})$$

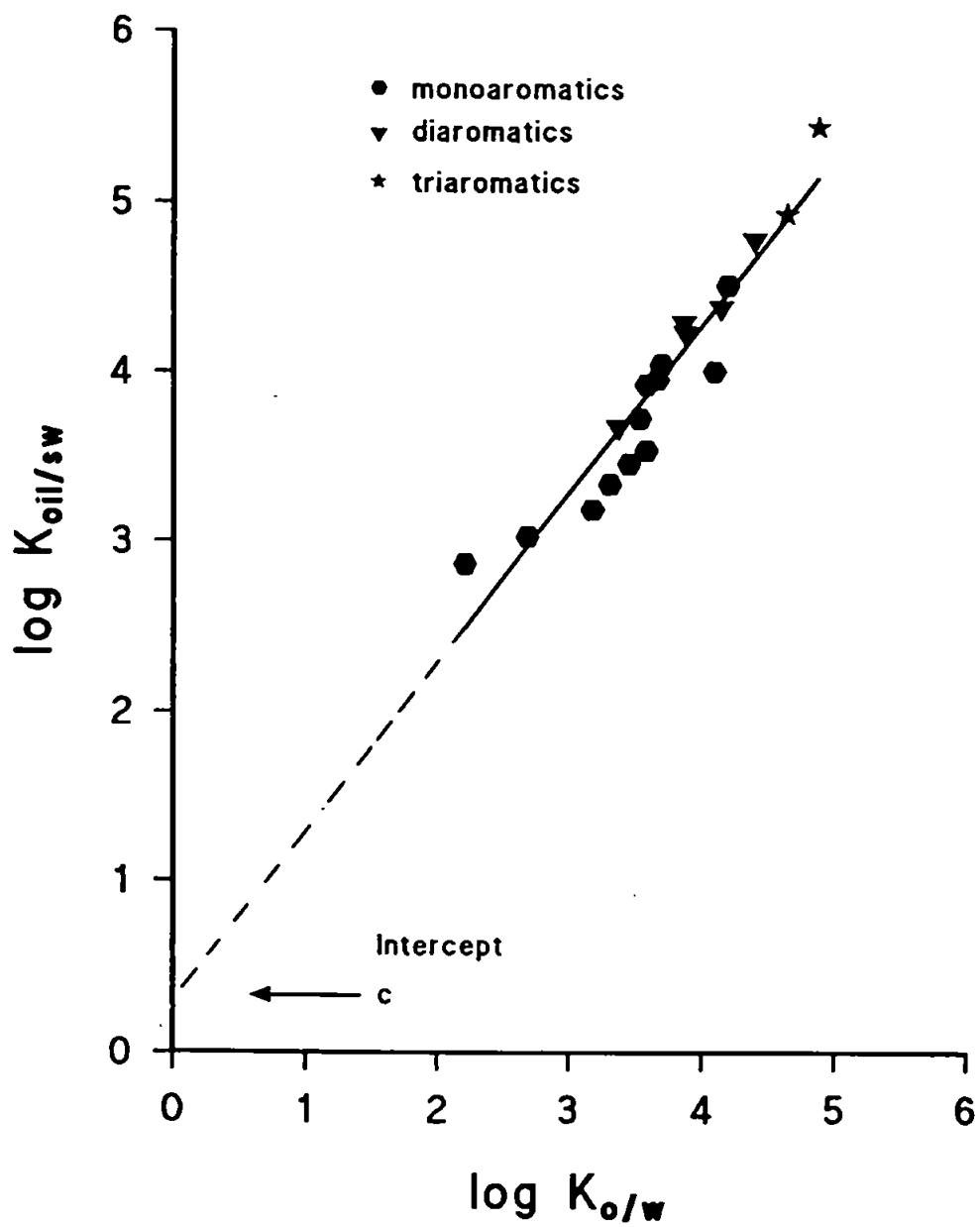


Figure 3.15 Correlation between $\log K_{oil/sw}$ and $\log K_{o/w}$ of SWSF components of Kuwait crude oil.

Table 3.14 Partition coefficient $K_{oil/sw}$ of the major compounds identified in the SWSF of Kuwait crude oil and in the oil used for the dissolution experiments.

NO.	Compound	Concentration		$K_{oil/sw}^a$	log $K_{oil/sw}$ Experimental	log $K_{o/w}$ Literature Value ^b
		SWSF $\mu\text{g mL}^{-1}$	Oil $\mu\text{g mg}^{-1}$			
1.	Benzene	1.3	1.23	736	2.87	2.13 ¹ , 2.21 ³ , 1.90 ⁵
2.	Toluene	4.3	5.74	1077	3.03	2.65 ¹ , 2.69 ⁴ , 2.51 ⁵
3.	Ethylbenzene	0.28	0.96	2914	3.46	3.13 ¹ , 3.15 ⁴ , 3.10 ⁵
4.	1,3-Dimethylbenzene					
	+	1.2	3.12	2188	3.34	3.20 ¹ , 3.14 ² , 3.31 ³
5.	1,4-Dimethylbenzene					
6.	1,2-Dimethylbenzene	0.82	1.52	1533	3.19	3.13 ¹ , 3.14 ² , 3.18 ³
7.	Isopropylbenzene	0.017	0.18	9176	3.96	3.66 ⁵ , 3.65 ⁵
8.	<i>n</i> -Propylbenzene	0.024	0.31	11250	4.05	3.69 ¹ , 3.65 ² , 3.68 ⁴
9.	1-Ethyl-3-methylbenzene					
	+	0.17	1.56	7959	3.90	
10.	1-Ethyl-4-methylbenzene					
11.	1,3,5-Trimethylbenzene	0.07	0.68	8429	3.93	3.58 ²
12.	1-Ethyl-2-methylbenzene	0.14	0.87	5357	3.73	3.53 ¹
13.	1,2,4-Trimethylbenzene	0.55	2.24	3480	3.54	3.58 ² , 3.78 ³ , 3.65 ⁵
14.	1,2,3-Trimethylbenzene	0.016	0.76	41625	4.62	3.55 ¹ , 3.58 ² , 3.61 ³
15.	<i>sec</i> -Butylbenzene	0.002	0.12	52500	4.72	
16.	1-Isopropyl-3-methylbenzene					
	+	0.011	0.31	24636	4.39	
17.	1-Isopropyl-4-methylbenzene					
18.	1-Isopropyl-2-methylbenzene	0.001	0.03	26000	4.41	
19.	1,3-Diethylbenzene	0.015	0.59	34400	4.54	

"continued..."

Table 3.14 "continued"

NO.	Compound	Concentration		$K_{oil/w}^a$	log $K_{oil/w}$ Experimental	log $K_{o/w}$ Literature Value ^b
		SWSF $\mu\text{g mL}^{-1}$	Oil $\mu\text{g mg}^{-1}$			
20.	1-Methyl-3-propylbenzene +					
21.	1,4-Diethylbenzene +					
22.	1,3-Dimethyl-5-ethylbenzene +	0.02	0.76	33250	4.52	4.19 ¹
23.	1,2-Diethylbenzene					4.19 ²
24.	1-Methyl-2-propylbenzene	0.016	0.43	23500	4.37	
25.	1,4-Dimethyl-2-ethylbenzene +	0.041	0.94	20024	4.30	
26.	1,3-Dimethyl-4-ethylbenzene					
27.	1,2-Dimethyl-4-ethylbenzene	0.017	0.38	19529	4.29	
28.	1,3-Dimethyl-2-ethylbenzene	0.017	0.25	12824	4.11	
29.	1,2-Dimethyl-3-ethylbenzene	0.004	0.03	6500	3.81	
30.	1,2,4,5-Tetramethylbenzene +	0.035	0.65	16200	4.21	4.11 ² ,4.27 ³
31.	1,2,3,5-Tetramethylbenzene					4.23 ³
32.	1,2,3,4-Tetramethylbenzene	0.053	0.62	10170	4.01	4.09 ³
33.	Naphthalene	0.089	0.5	4831	3.68	3.35 ¹ ,3.37 ⁴ ,3.30 ⁴
34.	2-Methylnaphthalene	0.029	0.66	19897	4.30	3.86 ¹
35.	1-Methylnaphthalene	0.031	0.62	17452	4.24	3.87 ¹ ,3.86 ²
36.	1+2-Ethylnaphthalene	0.002	0.14	61500	4.79	4.39 ¹ ,4.38 ²
37.	2,6-Dimethylnaphthalene +	0.005	0.47	82400	4.91	4.31 ¹ ,4.32 ⁵
38.	2,7-Dimethylnaphthalene					
39.	1,3-Dimethylnaphthalene +	0.01	0.58	50800	4.70	4.42 ¹ ,4.36 ² ,4.55 ⁵
40.	1,7-Dimethylnaphthalene					

"continued..."

Table 3.14 "continued"

NO.	Compound	Concentration		$K_{oll/sw}^a$	log $K_{oll/sw}$ Experimental	log $K_{o/w}$ Literature Value ^b
		SWSF $\mu\text{g mL}^{-1}$	Oil $\mu\text{g mg}^{-1}$			
41.	1,6-Dimethylnaphthalene	0.005	0.45	79000	4.89	
42.	2,3-Dimethylnaphthalene					4.40 ¹ , 4.36 ² , 4.18 ³
	+					
43.	1,4-Dimethylnaphthalene	0.006	0.36	52500	4.72	
	+					
44.	1,5-Dimethylnaphthalene					4.38 ¹ , 4.36 ²
45.	1,2-Dimethylnaphthalene	0.002	0.13	57000	4.75	
46.	1,3,7-Trimethylnaphthalene	0.001	0.21	184000	5.26	
47.	1,3,6-Trimethylnaphthalene	0.0016	0.38	208125	5.32	
48.	1,3,5-Trimethylnaphthalene					
	+	0.0018	0.35	170556	5.23	
49.	1,4,6-Trimethylnaphthalene					
50.	2,3,6-Trimethylnaphthalene	0.001	0.14	123000	5.09	
51.	1,2,7-Trimethylnaphthalene					
	+					
52.	1,6,7-Trimethylnaphthalene	0.0016	0.31	170000	5.23	
	+					
53.	1,2,6-Trimethylnaphthalene					
54.	1,2,4-Trimethylnaphthalene	0.0003	0.06	176667	5.25	
55.	1,2,5-Trimethylnaphthalene	0.0013	0.21	141538	5.15	
56.	Biphenyl	0.0025	0.07	24400	4.39	3.79 ² , 3.76 ¹ , 4.14 ³
57.	Dibenzothiophene	0.0005	0.16	280000	5.45	4.87 ²
58.	Phenanthrene	0.0008	0.08	87500	4.94	4.57 ¹ , 4.63 ² , 4.46 ³

^a see Table 3.12

^b Literature values in bold were used in Figure 3.15

¹ Miller *et al.* (1985)

² Yalkowsky *et al.* (1983)

³ Govers and Evers (1992)

⁴ Wasik *et al.* (1983)

$$\begin{aligned}
 K_{\text{oil/sw}} / K_{\text{o/w}} &= 10^6 \\
 K_{\text{oil/sw}} &= K_{\text{o/w}} \times 10^6 \\
 &= K_{\text{o/w}} \times 10^{0.28}
 \end{aligned}$$

The conclusions which can be drawn on the basis of the above derived relationships between $K_{\text{oil/sw}}$ and $K_{\text{o/w}}$ are :

(1) Partition of individual hydrocarbon between oil phase and seawater follows a similar hydrophobic/hydrophilic mechanism to that which occurs between octanol and water, and thus conforms to a linear free-energy relationship (LFER) [i.e. partition coefficients between different organic phase-water systems are related (see Shwarzenbach *et al.*, 1993)]. Therefore, the LFER as expressed in equation 5 can be used to estimate the $K_{\text{oil/sw}}$ value of a particular compound if its $K_{\text{o/w}}$ is known (or *vice versa*).

(2) The good correlation with a slope of 1.0 found between $\log K_{\text{oil/sw}}$ and $\log K_{\text{o/w}}$ implies that the partitioning of individual hydrocarbon is controlled primarily by its intrinsic hydrophobicity rather than by the salt content of the water or the nature of the organic phase (see Lyman, 1982).

(3) Use of equation 1 allows calculation of the quantity of an individual hydrocarbon that may be dissolved following an oil spill over seawater.

It must be noted that the results obtained here for $K_{\text{oil/sw}}$ apply only to oils that remain primarily in a surface film, such as occurs under calm sea conditions. When oil droplets are dispersed through the water column by rough weather, dissolution rates are much higher and may be independent of $K_{\text{oil/sw}}$. Other weathering processes (e.g. volatilisation,

emulsification, degradation) and their selectivity will also affect the evolving composition of SWSF following an oil spill. Photooxidation can alter oil composition and can result in the production of additional water soluble toxicants (see Chapter 5). It can also increase oil density sufficiently to cause it to sink and dispersal may occur as a result. However, the partition equilibrium between an oil layer and seawater is attained at different rates by different oil hydrocarbons. Therefore mixing times longer or shorter than 5 days, or different mixing rates, will result in SWSF with partition coefficients different to those presented here. Previous studies showed that when mixing rates or time vary, oil in water concentration also varies (e.g. Boylan and Tripp, 1971; Anderson *et al.*, 1974).

General Expression to Predict the Quantity of Hydrocarbon Partitioned into Seawater following an oil spill

The equation relating $K_{oil/sw}$ allows one to predict the solubilisation of individual hydrocarbons in various oil spill scenarios. Consider an oil spill M (tons = 10^6 g) of Kuwait crude oil (ρ 0.878 g mL⁻¹) of area A (km² = 10^6 m²) in coastal sea of Z (m) average depth and a compound of interest (y) in the oil, then;

$$\begin{aligned} \text{Volume (L) of oil} &= v_{oil} = M/\rho \\ &= M * 10^6 \text{ g} / 0.878 \text{ g mL}^{-1} \\ v_{oil} \text{ (L)} &= 1.14 * 10^3 M \text{ } \underline{\hspace{1cm}} \text{ (6)} \end{aligned}$$

$$\begin{aligned} \text{Volume of seawater } v_{sw} \text{ (L)} &= A * 10^6 \text{ (m}^2\text{)} * Z \text{ (m)} * 10^3 \text{ L/m}^3 \\ v_{sw} \text{ (L)} &= A * Z \text{ (10}^9\text{)} \text{ L } \underline{\hspace{1cm}} \text{ (7)} \end{aligned}$$

Consider:

x_{sw} mass (g) of component y dissolved in seawater

x_{oil} mass (g) of component y remaining in oil

x_t total (original) mass (g) of component y in oil

since,

$$x_t = x_{sw} + x_{oil}$$

therefore $x_{oil} = x_t - x_{sw}$

and $K_{oil/sw} = (m_{oil}/v_{oil}) / (m_{sw}/v_{sw}) \text{ _____ (1)}$

substituting in equation 1;

$$K_{oil/sw} = \frac{(x_{oil}/v_{oil})}{(x_{sw}/v_{sw})} = \frac{(x_t - x_{sw})}{v_{oil}} * \frac{v_{sw}}{x_{sw}}$$

$$= \frac{(x_t * v_{sw}) - (x_{sw} * v_{sw})}{(v_{oil} * x_{sw})}$$

$$= \frac{(x_t * v_{sw})}{(v_{oil} * x_{sw})} - \frac{(x_{sw} * v_{sw})}{(v_{oil} * x_{sw})}$$

$$= \frac{(x_t * v_{sw})}{(x_{sw} * v_{oil})} - \frac{v_{sw}}{v_{oil}}$$

or $\frac{(x_t * v_{sw})}{(x_{sw} * v_{oil})} = K_{oil/sw} + \frac{v_{sw}}{v_{oil}} = \frac{(K_{oil/sw} * v_{oil}) + v_{sw}}{v_{oil}}$

inverting

$$\begin{aligned}
 \frac{(x_{sw} * v_{oil})}{(x_t * v_{sw})} &= \frac{v_{oil}}{(K_{oil/sw} * v_{oil}) + v_{sw}} \\
 x_{sw} &= \frac{(x_t * v_{sw})}{(K_{oil/sw} * v_{oil}) + v_{sw}} \\
 \text{or } x_{sw} &= \frac{\frac{(x_t * v_{sw})}{v_{sw}}}{\left(\frac{(K_{oil/sw} * v_{oil}) + v_{sw}}{v_{sw}} \right)} \\
 &= \frac{x_t}{\left(\frac{(K_{oil/sw} * v_{oil})}{v_{sw}} \right) + 1} \quad (8)
 \end{aligned}$$

$$\text{Let } \frac{v_{oil}}{v_{sw}} = v_r \quad (9)$$

Substituting 9 into equation 8;

$$x_{sw} = \frac{x_t}{(K_{oil/sw} * v_r) + 1} \quad (10)$$

Where $x_t(g) = M$ (mass of oil tons) * P_x * 10^6 (g/ton)

P_x = proportion (w/w) of oil accounted for by hydrocarbon component y

And by substituting 6 and 7 into equation 9;

$$v_r = \frac{1.14 * 10^3 * M}{A * Z * 10^9} = \frac{1.14 * 10^{-6} * M}{A * Z}$$

Example

Consider spill of 10 tons of Kuwait crude oil over 1 km² of sea, average depth 5 m, applying equation 10, the quantity of benzene dissolved in seawater (x_{sw}); for benzene, concentration (Table 3.11) P_x :

$$= 1.23 \mu\text{g mg}^{-1} \text{ oil} \equiv 1.23 * 10^{-3} \mu\text{g g}^{-1} \text{ oil}$$

hence

$$x_t = 10 * 1.23 * 10^{-3} * 10^6$$

and

$$v_r = \frac{1.14 * 10^{-6} * 10}{1 * 5} = 2.28 * 10^{-6}$$

since

$$K_{\text{oil/sw}} = 736 \text{ (see Table 3.12)}$$

therefore by substituting the values of x_t , v_r and $K_{\text{oil/sw}}$ into equation 10;

$$\begin{aligned} x_{sw} \text{ (g)} &= \frac{(10 * 1.23 * 10^{-3} * 10^6)}{(736 * 2.28 * 10^{-6}) + 1} \\ &= \frac{(1.23 * 10^4)}{(0.001678 + 1)} \\ &= 12,279 \text{ g benzene solubilised into a volume of 5 million m}^3 \\ &\quad (10^6 \text{ m}^2 * 5 \text{ m}) \text{ of seawater.} \end{aligned}$$

3.5 Conclusions

A reliable method for the quantification of components in SWSF was developed and optimised. Attention to the efficient recovery of components and the development of an appropriate analysis method required the use of *n*-pentane for sample extraction with the addition of the correct amount of deuterated internal standards and a controlled evaporation using a micro Kuderna-Danish evaporative concentrator. The method was further optimised for the final concentration, the storage conditions which best preserved the integrity of extracts awaiting analysis and the reproducibility of analysis.

Detailed examination of a laboratory equilibrated seawater fraction of a Kuwait crude oil confirmed previous studies of various crude oils and showed that under conditions of low stirring rates, a selective process involving the dissolution of low-medium aromatic hydrocarbons occurred. However, the results reported here extend previous observations on the chemical composition of a seawater soluble fraction of crude oil. The chemical analyses using GC-MS with cryogenic cooling revealed more classes of compounds and gave more detail on the isomer distribution of the major groups than has been previously recorded. As a result more than 50 compounds were identified and quantified and the characterised SWSF can be regarded as a suitable substrate for controlled photodegradation experiments.

As would be expected from the solubility data, benzene and toluene were the most abundant components in the SWSF. A group of higher alkylbenzenes (C_2 - C_4) were also abundant but in lower concentration. In addition, an extensive range of alkylnaphthalenes (C_0 - C_3) were identified, although at much lower concentrations. Minor components such

as biphenyl, phenanthrene, dibenzothiophene and phenols were also observed.

The concentration of components identified in the SWSF was compared with their concentration in the fresh oil and the partition coefficient between the oil and seawater ($K_{oil/sw}$) was calculated. Compounds which had a high concentration in water (i.e. benzenes) were those which possessed low partition coefficient values. In contrast, compounds which had high $K_{oil/sw}$ (i.e. alkylnaphthalenes) were present only in very low concentration and the major mass remains in the oil phase. This demonstrates the role that partitioning plays in determining the attainable aqueous concentrations for a given initial concentration of the component in the oil phase following oil spillage. On the basis of the quantitative dissolution and $K_{oil/sw}$ data, it can be concluded that the dissipation of hydrocarbon components from spilled light/medium oil, through leaching and mixing into the aqueous phase would result in a continual selective dissolution of oil components, particularly low molecular weight aromatic hydrocarbons.

CHAPTER FOUR

CHAPTER FOUR

CONSTRUCTION OF AN IRRADIATION SYSTEM AND PHOTODEGRADATION OF PHENANTHRENE AS A SWSF MODEL COMPOUND

4.1 Introduction

Petroleum components released to the marine environment are susceptible to alteration by several processes including biodegradation and photodegradation (reviewed by Jordan and Payne, 1980). The most studied of these two processes is biodegradation (e.g. Kennicutt, 1988; Oudot and Dutrieux, 1989). Photodegradation was for some time considered to be of little importance compared to other weathering processes. However, microbial degradation may be slow in tropical and subtropical latitudes when nutrients are limited and photodegradation may then assume greater importance under conditions of intensive solar radiation (Ehrhardt, 1987). In addition, Literathy *et al.* (1989) showed that in waters of the Arabian Gulf, whilst *n*-alkanes, mono- and diaromatic compounds were easily metabolised by bacterial degradation, polyaromatic hydrocarbons (PAH) were mostly oxidised by photodegradation. Photodegradation was even found to enhance biodegradation by solubilising the oil components. In particular, the oxidised products from photooxidation of PAH (Lee and Ryan, 1983) and from alkyl-substituted benzenes (Rontani *et al.*, 1985; 1987) were used by microorganisms in biological oxidation processes.

Payne and Phillips (1985) reviewed studies related to petroleum photodegradation carried out both in the laboratory and in the field up to 1984. The review revealed the limited

nature of research in this area with few studies giving consideration to simulation of realistic environmental conditions. It was apparent that research was needed in a number of areas. In particular, the characterisation of the products derived from the photooxidation of petroleum, their toxicity and their fate and an improved understanding of the photochemical transformation in the environmental weathering of oil was needed.

Since then, Ehrhardt and coworkers have contributed significantly to an understanding of the consequences of photolytic processes on a variety of pure hydrocarbons under solar and simulated solar conditions (Ehrhardt and Petrick, 1984; 1985; Ehrhardt *et al.*, 1992). These researchers have also detected the products of photooxidation of fossil fuels in seawater from Bermuda (Ehrhardt, 1987) and the upper Arabian Gulf (Ehrhardt and DouAbul, 1989), where strong sunlight is likely to play an important role in the degradation of pollutant hydrocarbons.

Other photodegradation studies have been carried out on polyaromatic hydrocarbons (PAHs) (e.g. Patel *et al.*, 1978; Zepp and Schlotzhauer, 1979; Paalme *et al.*, 1990) and other aromatic compounds (Mabey *et al.*, 1983; Aksnes and Iversen, 1983) under various experimental conditions to try to predict the influence of sunlight on the fate of these pollutants. Such compounds may find their way into water bodies as a result of oil spills, industrial discharges and a variety of other sources.

A summary of some of these studies is presented in Table 4.1. Other summaries are provided by Payne and Phillips (1985) and Boehm (1987).

Table 4.1 Summary of Photodegradation studies under various irradiation conditions.

Substrate	Light Source & Wavelength	Sensitizer Used	Reaction Rate & $t_{1/2}$	Product Identified	Mechanism Proposed	Comments	References
Kuwait crude oil + chemical dispersant 1:5 (dispersant: oil)	> 280 nm ambient daylight illumination	-----	-----	Indication of the formation of some oxygenated compounds	-----	<p>Significant decrease in the quantities of fluorescing compounds (polycyclic aromatics) were observed using fluorescence scanning method.</p> <p>Photooxidation was fast resulted in an increase of fluorescence in the monocyclic aromatic range between 250-275 nm.</p> <p>Photooxidation changed the absorption of several bonds in the 1300-1800 cm^{-1} wave number range corresponding to <i>n</i>-alkanes photooxidation as measured by FT-IR.</p>	Literathy <i>et al.</i> (1989)

"Continued..."

Table 4.1 "Continued"

Substrate	Light Source & Wavelength	Sensitizer Used	Reaction Rate & $t_{1/2}$	Product Identified	Mechanism Proposed	Comments	References
<i>n</i> -Pentadecane in purified natural seawater	Natural sunlight	Anthraquinone	-----	<i>n</i> -Heptanone-2 <i>n</i> -Octanone-2 + <i>n</i> -decane-1 <i>n</i> -Nonanone-2 + <i>n</i> -undecene-1 <i>n</i> -Decanone-2 + <i>n</i> -dodecene-1 <i>n</i> -Undecenone-2 <i>n</i> -Dodecenone-2 <i>n</i> -Pentadecane Mixture of <i>n</i> -pentadecanone-6, -7 and -8 <i>n</i> -Pentadecanone-5 <i>n</i> -Pentadecanone-4 Pentadecanone-3 Pentadecanone-2	<p>The excited triple-state anthraquinone reacted with molecular oxygen forming peroxy radicals which stabilize themselves as hydroperoxides by in cooperation of a hydrogen atom.</p> <p>The hydroperoxide undergo homolytic cleavage at the o-o bond. The resulting oxy radicals then start reaction sequences forming stable products.</p> <p>These reaction sequences include reaction with molecular oxygen to form stable ketones, or by cyclic electron rearrangements if γ-hydrogen atom are available to form 1-alkenes and alkoxy radicals.</p> <p>The latter either yield methyl ketones and H_2O^\bullet radicals upon reaction with molecular oxygen or undergo further decomposition as long as γ-hydrogen atom are available.</p>	The generation of acetone and H_2O^\bullet radicals as products of the degradation sequences was suggested to offer an additional explanation for their occurrence in seawater.	Ehrhardt & Petrick (1985)

"Continued..."

Table 4.1 "Continued"

Substrate	Light Source & Wavelength	Sensitizer Used	Reaction Rate & $t_{1/2}$	Product Identified	Mechanism Proposed	Comments	References
Solution of dispersed crude oils and benzo (a) pyrene in sterilized seawater	Solar radiation (29 °N latitude)	-----	$t_{1/2}$ of B(a)p was 0.14 hr in the chemically dispersed sample, 0.34 hr in the physically dispersed sample	Non fluorescent high molecular weight breakdown products	-----	Reactor geometry, level of dispersion of compounds and the presence of particulate matter influenced significantly the reaction rate. B(a)p was used as a model mixture of fluorescing compounds in seawater. Significant decrease in the fluorescence intensities in the crude oil/B(a)p mixture were observed but the total extracted material remained unchanged which suggested transformation of fluorescing compounds to other non-fluorescing compounds.	Literathy <i>et al.</i> (1991)

"Continued..."

Table 4.1 "Continued"

Substrate	Light Source & Wavelength	Sensitizer Used	Reaction Rate & $t_{1/2}$	Product Identified	Mechanism Proposed	Comments	References
Authentic mixture of PAH: Naphthalene, 1-Methylnaphthalene, 2-Methylnaphthalene, Phenanthrene, Anthracene, 9-Methylanthracene, 9,10-Dimethylanthracene, Pyrene, Fluoranthene, Chrysene, Naphthacene in water	313 313 313 313 366 366 366 313, 366 313, 366 313 436 from a 450-W medium pressure mercury lamp.	-----	71 hr 22 hr 54 hr 8.4 hr 0.75 hr 0.13 hr 0.35 hr 0.68 hr 21 hr 4.4 hr 0.034 hr	-----	-----	Data obtained from the lab experiment were <u>computed</u> and used to <u>predict</u> $t_{1/2}$ of the PAH, reported here at latitude 40 °N midday, midsummer.	Zepp and Schlotzhauer (1979)
Authentic mixture of PAH: Fluoranthene (FLA) Pyrene (PY) Benzo(a)anthracene (BaA) Benzo(a)pyrene (BaP) in high purity water	Sunlight 42 °N latitude	-----	FLA = 0.07 hr ⁻¹ / 10 hr PY = 0.82 hr ⁻¹ / 0.85 hr BaA = 1.00 hr ⁻¹ / 0.67 hr BaP = 1.40 hr ⁻¹ / 0.48 hr	-----	-----	Rates and $t_{1/2}$ of studied PAH agreed with previously reported rates for average mid-summer sunlight.	Picel <i>et al.</i> (1985)

"Continued..."

Table 4.1 "Continued"

Substrate	Light Source & Wavelength	Sensitizer Used	Reaction Rate & $t_{1/2}$	Product Identified	Mechanism Proposed	Comments	References
Homogenous and surface film of alkylbenzene in either purified seawater or Milli-Q water	150 W high-pressure argon lamp and solar radiation	Anthraquinone and anthracene	-----	Ethylbenzene 1-Phenylethanone D, L-1-Phenylethanol Benzaldehyde <i>n</i> -Propylbenzene 1-Phenyl-1-Propanone D,L-1-Phenyl-1-propanol Benzaldehyde <i>n</i> -Butylbenzene 1-Phenyl-1-butanone D,L-1-Phenyl-1-butanol Benzaldehyde 1-Phenylethanone <i>n</i> -Pentylbenzene 1-Phenyl-1-pentanone D,L-1-Phenyl-1-pentanone Benzaldehyde 1-Phenylethanone <i>n</i> -Nonylbenzene 1-Phenyl-1-nonanone Benzaldehyde 1-Phenylethanone 1-Phenyl- <i>n</i> -tridecane 1-Phenyl-1-tridecanol D,L-1-Phenyl-1-tridecanol Benzaldehyde 1-Phenylethanone <i>n</i> -Undecene-1 <i>n</i> -Dodecane <i>n</i> -Decanal	Anthraquinone is excited to first singlet state by light, undergo inter-system crossing to form first triplet state, which then abstract a benzylic hydrogen atom from an alkyl benzene resulting in benzylic radical. This radical react with O ₂ to form a peroxy radical which initiate sequential reactions forming the products identified in this study.	No photodegradation took place without photosensitizer under sunlight. The chemical nature of photooxidation products was independent of the reaction medium, purified natural seawater or distilled Milli-Q water. No products Yield were given for substrate irradiated under artificial light to compare with yields obtained under natural sunlight. The same products were obtained in homogeneous aqueous solution as in two-phase system.	Ehrhardt & Petrick (1984)

One area of contention with respect to the environmental relevance of several of these studies is the use of an artificial light source which emits high energy UV light, usually between 185-295 nm. Wavelengths of light in this region give much faster photodegradation rates and much higher product yields than the less energetic wavelengths present in ambient sunlight (Hansen, 1975). Thus, product distribution as well as the product yield may differ from that found in the natural environment. Care should therefore be exercised in the interpretation of photoreactivity and phytotoxicity studies of oil or oil related compounds which have been based on the use of an artificial light source (Sydnes and Burkow, 1985).

Light is a crucial factor associated with degradation of oil pollutants in the marine environment (reviewed by Zafiriou, 1977 and Zika, 1981). For moderately high solar altitudes and mixed layer depth seas, about 80-90 % of the incident solar radiation can be absorbed as shown in Figure 4.1 (Roof, 1982). Therefore, oil components in a slick or in the water column (SWSF) can absorb some of this light at different wavelengths and then undergo photochemical transformation.

Miller (1983) mentioned other environmental factors important to photodegradation, such as the presence of molecular oxygen and other oxidants such as peroxides. In a study carried out by Mill *et al.* (1981), the role of oxygen on the photolysis rate constant showed great variation. For example, purging an aqueous solution of dibenzothiophene with nitrogen had no significant effect on the photolysis rate constant, indicating that oxygen was not contributing to the photodegradation of dibenzothiophene. The opposite was shown for benzo[a]anthracene, where purging with nitrogen strongly inhibited photolysis. Moreover, the concentration and availability of oxygen was found to alter both the

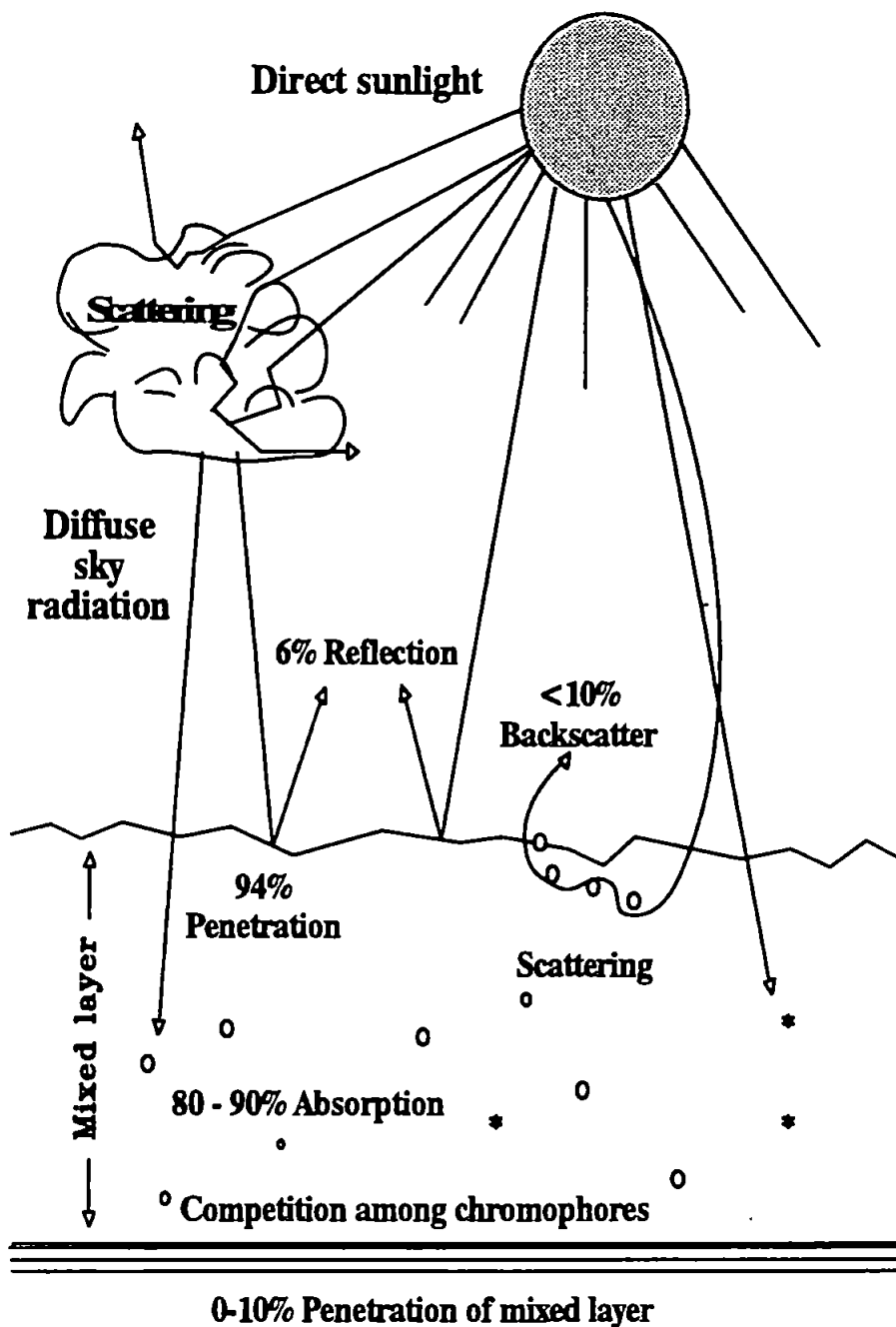


Figure 4.1 "Black sea" model. Numerical values are chosen to be typical for moderately high solar altitude and mixed layer depths on the order of tens of metres. Various shaped symbols in the mixed layer represent different chromophores, irrespective of dissolved or particulate state (Roof, 1982).

products and the product yield derived from anthracene photolysed in water (Sigman *et al.*, 1991).

Certain dissolved organics in natural waters, such as humic substances (reviewed by Zepp, 1988) may also affect the photooxidation reaction. They can photosensitise a variety of reactions and thus become an important determinant of the photochemical pathway of some compounds (Zepp *et al.*, 1985). They can also be light-absorbing materials which slow the photolysis rate for compounds which undergo direct photooxidation (Mill *et al.*, 1981).

Other environmental factors that affect photolysis in water are salinity (Fukuda *et al.*, 1988) and temperature (Thominette and Verdu, 1984a) both of which are proportional to photolysis rate. The presence of suspended matter was found to reduce the photolysis rate of compounds through light attenuation and partitioning to particulate material (Miller and Zepp, 1979). Another important parameter is the irradiation time, which may determine the photodegradation rate of a compound and influence the yield of the transformation products (Sigman *et al.*, 1991).

Photodegradation studies carried out under natural conditions are of course more representative of real environmental situations. However, the complexity of environmental constituents, as discussed above, in addition to the complexity of the substrate under investigation (e.g. crude oil, oil extract) and the variety of parameters that could interact (e.g. other competing processes such as biodegradation and chemical oxidation), make observations very difficult to interpret (e.g. Tjessem and Aaberg, 1983). Laboratory models, with a limited number of controlled parameters, are an alternative (e.g. Aksnes and Iversen, 1983). If careful consideration is given to the implementation of experimental

methods relevant to natural environmental conditions, then the data gained may be more closely allied to the actual situation. Laboratory methods can then be validated with field studies. For example, Patel *et al.* (1979) found that photoproducts which were formed by laboratory photooxidation of dibenzothiophene were also present in an oil slick sample obtained from a field location following the Amoco Cadiz oil spill.

4.1.1 Experimental Approach

A number of experimental conditions must be considered when carrying out laboratory simulated photooxidation studies. Amongst the most important of these are the selection of an appropriate light source and filter system and use of UV-transparent quartz reaction cells that allow solutions of test chemicals to be irradiated reproducibly with uniform and constant amounts of light. The temperature of the reaction cells must be controlled and precautions must be taken to prevent the loss of chemicals from the reaction cells by processes other than photooxidation. For example, biodegradation and volatilisation can be eliminated or minimized by using sterile techniques (Paalme *et al.*, 1990) and by allowing a minute air space in the reaction cells (Literathy *et al.*, 1989).

The following sections will discuss further these parameters.

Light Source

Natural sunlight comprises a broad range of light wavelengths. Wavelengths below 290 nm, which are the most energetic, are largely absorbed by ozone in the upper atmosphere (Giese, 1976). Thus, for photochemical reactions taking place at the surface of earth, wavelengths greater than 290 nm can be considered to be of most importance.

Ideally, solar radiation should be used for experiments in environmental photochemistry. However, restrictions arising from changes in intensity both on a daily and a seasonal basis, and variation in wavelength distribution which depends on latitude and general weather conditions makes natural sunlight inconvenient to use (Kirk, 1986). Artificial radiation sources are usually preferred as they offer greater stability and reproducibility than outdoor studies (e.g. Klein and Pilpel, 1974a; ThomINETTE and Verdu, 1984a,b; Fukuda *et al.*, 1988). Furthermore, artificial "filtered" lights which simulate the solar radiation (e.g. xenon lamps) are advantageous because they shorten the irradiation time and maximise the yield of photoproducts thereby improving the accuracy of the identification and measurement of photoproducts as compared with sunlight. However, consideration must be given to the degradation rates and half-lives obtained from these studies when extrapolating the findings to the real environment.

Figure 4.2 shows the solar spectrum and the major artificial radiation sources used in laboratory photodegradation simulation studies. These included xenon arcs (filtered and unfiltered), mercury lamps (low, medium and high pressure); black light fluorescent and day-light lamps (a review of the conventional light sources is given by Gould, 1989). Most of these lamps emit shorter-wavelength light which is more energetic radiation than those wavelengths available in the solar radiation that reaches the earth's surface (Zepp, 1982). Consequently, filtering is required to block off light of < 300 nm in order to simulate the filtering effect of the earth's ozone layer. This can be achieved by various means, such as employing a borosilicate glass filter (Draper, 1985) or using chemical solutions (Leifer, 1988).

The lamp that more closely simulates natural sunlight is the xenon arc (Figure 4.2). Not

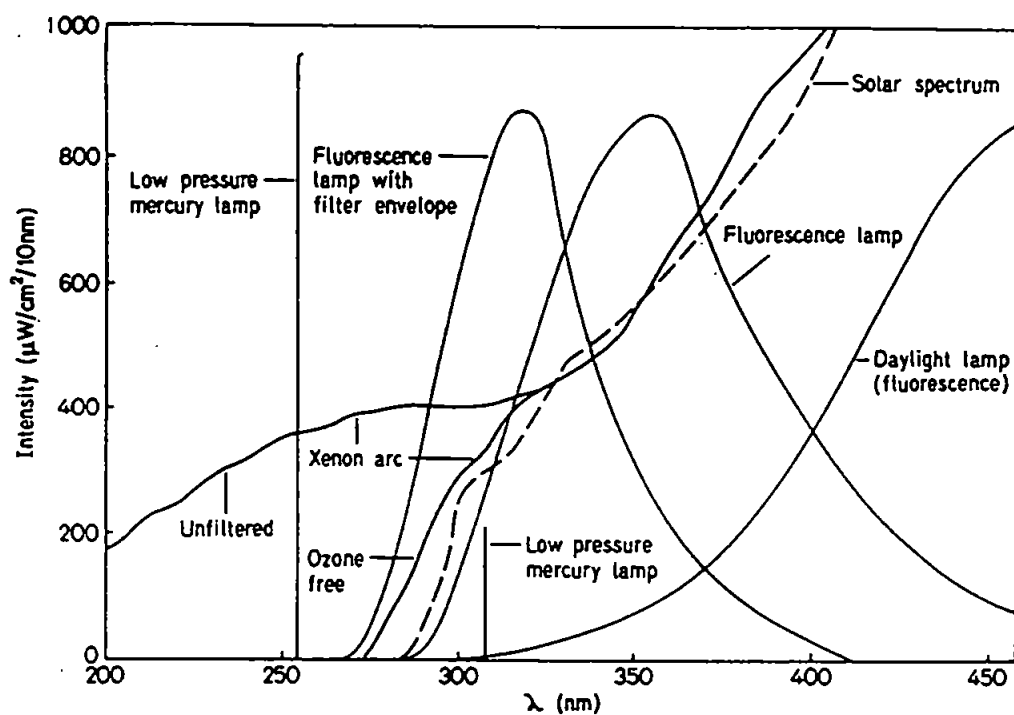


Figure 4.2 Spectral distribution of the emission of the most important artificial radiation sources (Roof, 1982).

only does its spectral distribution best resemble that of sunlight, but also its light intensity is the closest to those of natural light when filtered to remove wavelengths < 300 nm. It is perhaps less used in photolysis studies than is desirable because it is not as economical and practical as other light sources such as mercury lamps. The latter are the conventional radiation sources of classical organic photochemistry.

Light intensity is an important factor that affects photolysis rates. The importance of this factor was illustrated in a study in which the direct photolysis rate constant for three aromatic hydrocarbons (naphthalene, anthracene and naphthacene) irradiated under artificial light sources were compared to those under summer sunlight (Zepp, 1982). To emphasise the influence of light intensity upon the relative values (i.e. the ratios of rate constants in artificial light to those in summer sunlight), spectral irradiance from all light sources was normalised so that the flux for all light sources (filtered to remove wavelength < 300 nm) including sunlight, would be measured at the same UV region between 300–380 nm (Table 4.2). This study showed that when the ratio was > 1 the compound photolysed more rapidly with artificial light than with sunlight, a value of < 1 indicated that photolysis in sunlight was more rapid. Results obtained for the xenon lamp, although still higher by a factor of 2.6 (for naphthalene, < 1 for anthracene and naphthacene), were the closest to those of sunlight. Use of the other light sources either over- or underestimated the sunlight photolysis rate constants by a larger margin.

The intensity of the light source is one of the most critical factors associated with photochemical work. Therefore to be able to compare degradation rates between studies, the light intensity must be accurately known. Actinometers are devices used to measure light intensity and are classed as chemical (reviewed by Miller and Zepp, 1983) and

Table 4.2 Relative rate constants computed for direct photolysis of naphthalene, anthracene, and naphthacene with various light sources with spectral irradiance normalized so that integrated irradiance (300-380 nm) is the same for all sources^{a,b}.

Light Source	Naphthalene	Anthracene	Naphthacene
Summer sunlight ^c	1	1	1
Winter sunlight ^c	0.55	1.02	1.25
Sunlamp	11.6	0.55	0.12
Blacklight	0.17	1.13	0.043
Medium-pressure mercury lamp	12.7	0.57	0.31
Xenon lamp	2.6	0.94	0.65

^a The artificial light is assumed to be filtered so that wavelengths less than 295 nm are excluded.

^b For each compound, relative rate constants were computed by ratioing to the rate constant for direct photolysis at midday during summer, latitude 40 °N.

^c Midday, latitude 40 °N.

Source: Zepp (1982).

physical (Dupont *et al.*, 1990). The physical actinometers such as radiometers and spectroradiometers are easier and more convenient to use and were used to measure the light intensity of the xenon lamp used in this study.

Temperature Control

Temperature is also an important factor in assessing the rate constant for some photochemical reactions. The effect of temperature on the kinetic rate constant (k) can be expressed in the Arrhenius formula:

$$k = A e^{-E_a/RT}$$

Thus reaction rates may increase or decrease with temperature (Thominette and Verdu, 1984a). It has been determined that the reaction temperature should be controlled to ± 2 °C in order to obtain a reliable degradation rate (Leifer, 1988).

Other Experimental Factors

From an experimental viewpoint, it is useful to perform photolysis tests in homogeneous solutions that are well characterised and controllable. A homogeneous solution of the test chemical is best prepared at a concentration equal to or less than the water solubility. Using concentrations higher than the solubility limit may result in light attenuation either by the chemical or its transformation products which consequently affects photolysis (Zepp, 1982).

If the compound is not sufficiently soluble in water, polar co-solvents such as acetonitrile, ethanol or methanol are often used. These co-solvents have the advantage of being miscible with water and have refractive indices very close to that of water thus causing minimal

solvent effects (Leifer, 1988). The percentage of the co-solvent, however, should be kept at a minimum to minimise photolysis interference.

The purity of both the solvent and the compounds under investigation is also important because the presence of contaminants which have the ability to absorb light at similar wavelengths can lead to significant overestimation of photolysis rate. This process is known as "quenching". Glassware used in photolysis experiments must be free from contamination which could interfere with the photolysis and the identification of the photo-products.

The incorporation of dark control samples is essential; light should be totally excluded from these, for instance by wrapping the tubes with aluminium foil or any other suitable method. It is preferable to carry out a trial photodegradation experiment in order to determine the approximate rate constant of the test chemical and to verify the general experimental conditions (e.g. Literathy *et al.*, 1989).

4.1.2 Mechanism of Petroleum Photooxidation

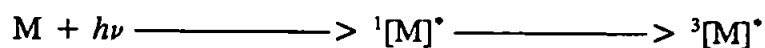
Photooxidation of a hydrocarbon mixture containing polynuclear aromatics may proceed through two photo-reaction pathways: one in which the absorbing compound undergoes change directly (direct photooxidation); and the other in which another substrate (photosensitizer) absorbs light and transfers energy to a compound which does not itself absorb sunlight but which then undergoes photooxidation (indirect or sensitised photooxidation) (Leifer, 1988).

For direct photooxidation to take place, a spectral overlap is required between the radiation from a light source and the light absorption by the chemical. In general, chemicals that absorb at wavelengths > 300 nm, such as polycyclic aromatic hydrocarbons, have the potential to undergo rapidly direct photolysis under either sunlight or other representative light sources.

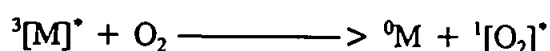
In the absence of overlap between the absorption wavelength of the substrate and the light source (i.e. when the substrate absorbs at $\lambda < 300$ nm), indirect photooxidation in the presence of a sensitizer can lead to a number of oxygenated products. Mononuclear aromatics being inactive in the near-UV region, mostly undergo indirect photooxidation. In all photooxidation mechanisms, aromatic compounds have an essential function, and the initial steps can be described as follows:

1. The formation of singlet oxygen by energy transfer after initial excitation by light. In this case, singlet oxygen, which is formed by transfer from an oxygen molecule in its triplet state, can combine directly with the polycyclic aromatic hydrocarbon to form PAH peroxides which are in turn photolysed to give other oxygenated compounds such as acids, ketones and alcohols (Thominette and Verdu, 1984a,b; Sigman *et al.*, 1991). This reaction is presented schematically as follows:

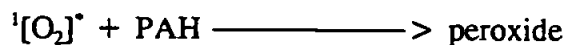
mechanism 1 : by singlet oxygen



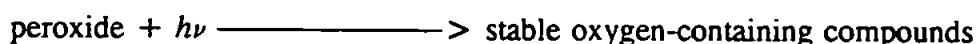
where M = a molecule absorbing in near-UV (e.g. humics)



where $^1[\text{O}_2]^*$ = excited singlet oxygen

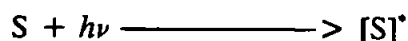


where PAH = polycyclic aromatic hydrocarbon

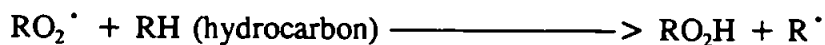
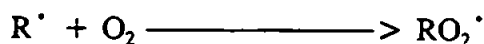
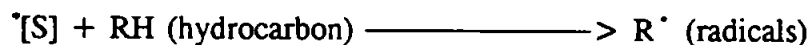


2. The photochemical formation of free radicals in the presence of a photosensitiser. Photosensitisation occurs when the acceptor molecule (i.e. hydrocarbon) is in contact with an excited donor species (i.e. photosensitiser). The result of this reaction is the formation of a radical which can combine with ground-state oxygen and then react further with a hydrocarbon (which has abstractable non-aromatic hydrocarbons), forming photoproducts (e.g. Gesser *et al.*, 1977; Larson *et al.*, 1979; Ehrhardt and Petrick, 1984; 1985). This reaction is represented by the following :

mechanism 2: by radicals:



where S = photosensitiser molecule

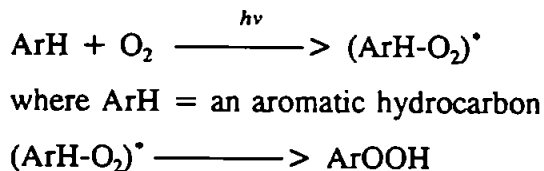


A number of sensitisers have been involved in petroleum related photooxidation studies. Anthracene, a naturally occurring very minor compound in petroleum, and anthraquinone which forms from anthracene by oxidation in natural waters, have been used to sensitise

the photooxidation of alkylbenzenes (Ehrhardt and Petrick, 1984) and *n*-pentadecane (Ehrhardt and Petrick, 1985). Compounds suitable as sensitizers must absorb energy at longer wavelengths than those at which the acceptor absorbs. This results in the formation of the singlet or triplet state with sufficient lifetime and energy to initiate the free-radical chain reaction shown above (Roof, 1982).

3. The formation of charge transfer complexes (CTC) between aromatic hydrocarbons and oxygen leads to a shift in the absorption band towards longer wavelengths, thus facilitating the formation of hydroperoxides. Such a reaction was reported for the photodegradation of toluene and xylene (Sydnes *et al.*, 1985a) and diphenylmethane (Aksnes and Iversen, 1983).

mechanism 3: by formation of charge-transfer complex:



4.1.3 Kinetics of Photodegradation

Experiments have shown that when the concentrations of reactants are low, as is frequently the case with environmental samples, first-order rate expressions usually describe the kinetic data (Literathy *et al.*, 1989). The photolysis of individual compounds can be experimentally determined from the equation:

$$\ln [C_i(t)/C_i(0)] = -k_{p,i} t$$

where $C_i(t)$ = Concentration of compound 'i' at time 't'

$C_i(0)$	= Concentration of compound 'i' at time '0'
$k_{p,i}$	= First-order photodegradation rate constant of compound 'i'
t	= Irradiation time in days, hours, or minutes, or seconds.

The rate constant ($k_{p,i}$) of a photoreactive compound 'i' can be obtained graphically from plotting $\ln [C_i(t)/ C_i(0)]$ versus time of irradiation. The slope of the linear regression line will be the ($k_{p,i}$) value.

The half-life ($t_{1/2}$) of a compound 'i' corresponds to the time taken for 50% reduction in the initial concentration of the compound and can be calculated from the equation:

$$t_{1/2, i} = 0.693 / k_{p,i}$$

4.1.4 Photooxidation Products

The products of petroleum photooxidation include alcohols, ketones, aldehydes, acids, peroxides and hydroperoxides. The percent yield and type of products depends on the type and concentration of the initial substrate, light intensity and the reaction time (e.g. Gesser *et al.*, 1977; Larson *et al.*, 1979).

Incorporation of oxygen into hydrocarbons results in greater water solubility, thus increasing the toxicity of the water-soluble fraction. Payne and Phillips (1985) mentioned that photooxidation contributes more to toxicity than microbial degradation due to the formation of more water soluble products by the former process.

It has been shown that sunlight increases the toxicity of the water-soluble fraction of crude oil and petroleum products to algae (Lacaze and de Naide, 1976), bacteria (Pengerud *et al.*, 1984), marine invertebrates and fish (Scheier and Gominger, 1976). This increase has been attributed to the formation of a variety of oxygenated photoproducts but because of the complexity of the products formed, it was difficult to assign a role to any one particular product.

A variety of studies have shown that the potential exists for many PAH to cause photo-induced toxicity to marine organisms (e.g. Oris and Giesy, 1985; 1987; Kagan *et al.*, 1985). The results demonstrated that PAH with short phosphorescence life times are toxic, and photo-induced toxicity of PAH is inversely proportional to the lifetime of the excited triplet state.

The identification of the photo-products, either from a field or a laboratory study is complicated by the fact that these products are usually present in trace quantities. Consequently a large volume of water is required increasing the possibility of contamination and further complicating techniques, especially in field studies. Also, methods of analysis applied to oil spill samples are not designed to include the products of photooxidation which may consequently be incorrectly characterised (Burns, 1993).

The importance of including hydrocarbon oxidation products in environmental assessment studies has only recently been recognised. In fact, the level of these products can sometimes be significant enough to contribute to the overall toxicity of hydrocarbon contaminants (Burns *et al.*, 1990; Burns, 1993).

Compared to other physical processes, such as spreading and evaporation, photooxidation is a relatively slow process but nevertheless important in the longer term. In addition to enhancing the dispersion of oil spills by transforming the oil components to more water soluble ones, photooxidation is also responsible for the changes in the physical properties of exposed oil (Sokolov *et al.*, 1986). Non-viscous oil slicks spread as a result of photooxidation, whereas viscous oil contracts due to the formation of polymeric products (Klein and Pilpel, 1974a). The high viscosity of the oil can restrict diffusion of the oxidation products to the oil-water interface, which could lead to the formation of tarry residues that may eventually sink to the seabed. These changes are an important factor in oil slick dispersal.

Enhancing oil dissolution by forming more soluble oxygenated products was used in a new practical approach to assist the natural oxidation of oil in the aquatic environment (e.g. Rosenberg *et al.*, 1992; Wang *et al.*, 1992). In this approach, photocatalytic particles of titanium dioxide (TiO_2) immobilized on hollow glass beads, which is activated by absorbing UV-solar radiation, produce hydroxyl and hydroperoxyl radicals either by the oxidation of hydroxide ions in water or by the reduction of molecular oxygen from air. These chemical oxidation radicals attack oil to form hydroxyl, carbonyl and carboxylate oil products which are soluble in water. This provides a more rapid exposure of the products to degrading microorganisms in sea water. Although this method may have the potential for solar-assisted oxidation of oil slicks, further development is required before a full economic assessment of the method can be made.

In conclusion, it is evident from the literature that only limited research studies have been directed towards determining the effectiveness of sunlight in removing oil spills and related

components from the marine environment, or characterising and quantifying the accumulated photooxidation products.

4.2 Aims

Many previous laboratory based investigations have failed to take a complete account of the photo-degradation of petroleum compounds under conditions which reflect the natural environment (i.e. solar irradiation, temperature, natural seawater).

The aim of this stage of the research was to study the photodegradation kinetics of the characterised water-soluble fraction of Kuwait crude oil in the laboratory, by selecting experimental parameters which more closely approximated natural conditions.

The initial aims of this work were:

- 1- Development of a reproducible methodology for studying photodegradation kinetics, using a model oil aromatic compound (phenanthrene) to verify the irradiation system and establish the photolysis experimental method.
- 2- Definition of the kinetics of the photolysis of phenanthrene, and characterisation of the transformation photo-products.
- 3- Application of the established photolysis methodology to determine the photodegradation rates and half-lives of compounds of the characterised water-soluble fraction of Kuwait crude oil.

In this chapter, aim 1 and aim 2 will be discussed, whereas aim 3 will be dealt with in the next chapter.

4.3 Experimental

4.3.1 Materials

Phenanthrene (99.5% purity), fluorene (98%), fluorenone (97%), and 9,10-phenanthrenequinone (99%) were purchased from Aldrich Chemical Co. Ltd., England. 3,4-benzocoumarin (98%) was obtained from Aldrich Chemical Co. Milwaukee, U.S.A. 3-methylphenanthrene was provided by Professor Steve Rowland, Department of Environmental Sciences, University of Plymouth, Plymouth, U.K. Borontrifluoride/methanol (BF_3 /methanol) complex (99.5%) and iodomethane (CH_3I) reagent (99.5%) used for derivatisation, were obtained from Sigma Chemical Co. Ltd., and Aldrich Chemical Co. Ltd., respectively. Dimethyl sulfoxide (DMSO) (95%) was obtained from BDH chemicals.

The Suntest CPS xenon lamp was manufactured by Heraeus Instruments GmbH, Germany and was purchased from their distributor; Heraeus Equipment Ltd., Unit 9, Water Way, Brentwood, Essex CM15 9TB, U.K. The unit and its specifications are shown in **Appendix 2**.

The chiller thermo circulator unit model 05/CTCHG was purchased from Conair Churchill Ltd., Riverside Way Uxbridge, Middlesex, U.K. The specifications of the chiller unit are given in **Appendix 3**.

Quartz tubes (25 cm long; 2 cm o.d.; i.d. 1.8 cm; 19/26 socket ground silica joint) and quartz stoppers (hollow, projecting a further 2 cm, see **Figure 4.3**) were made by H. Baumbach & Co. Ltd., Ipswich, Suffolk, U.K.

The stainless steel tank used for holding the tubes under controlled temperature during irradiation, was kindly provided by Dr. John Leahey, Zeneca Agrochemicals, Jeallots Hill, Bracknell, Berkshire, U.K.

4.3.2 Preparation of Phenanthrene in Seawater Solution

The phenanthrene in seawater solution was prepared in a closed 1 L reagent flask, using 1 L filtered, sterilised seawater ($20 \text{ mg L}^{-1} \text{ HgCl}_2$) containing 0.8 mg of phenanthrene. For this, a standard stock solution of 4 mg mL^{-1} of phenanthrene in acetone was first prepared and then $200 \mu\text{L}$ was added to the seawater. The resultant concentration (0.8 mg L^{-1}) of the prepared solution was close to the reported solubility ($1\text{--}1.3 \text{ mg L}^{-1}$ at 25°C) of phenanthrene in water. The preparation was made in a dark fume cupboard. To eliminate air from the reagent flask after addition of the phenanthrene, the headspace was flushed with N_2 . This was done to prevent oxidation during preparation of the solution. The flask was then sealed using a 'Suba.Seal' (through which a 12" 22-gauge stainless steel sampling needle, with female luer hub and deflecting tip was inserted). Gentle shaking was used to mix the phenanthrene with the seawater. This arrangement ensured that phenanthrene in seawater was prepared and sampled in a closed system and avoided losses by volatilisation.

This phenanthrene stock solution was found to be stable for seven days, if stored in a cool, dark place. Before utilising the solution for irradiation, the flask was placed in a

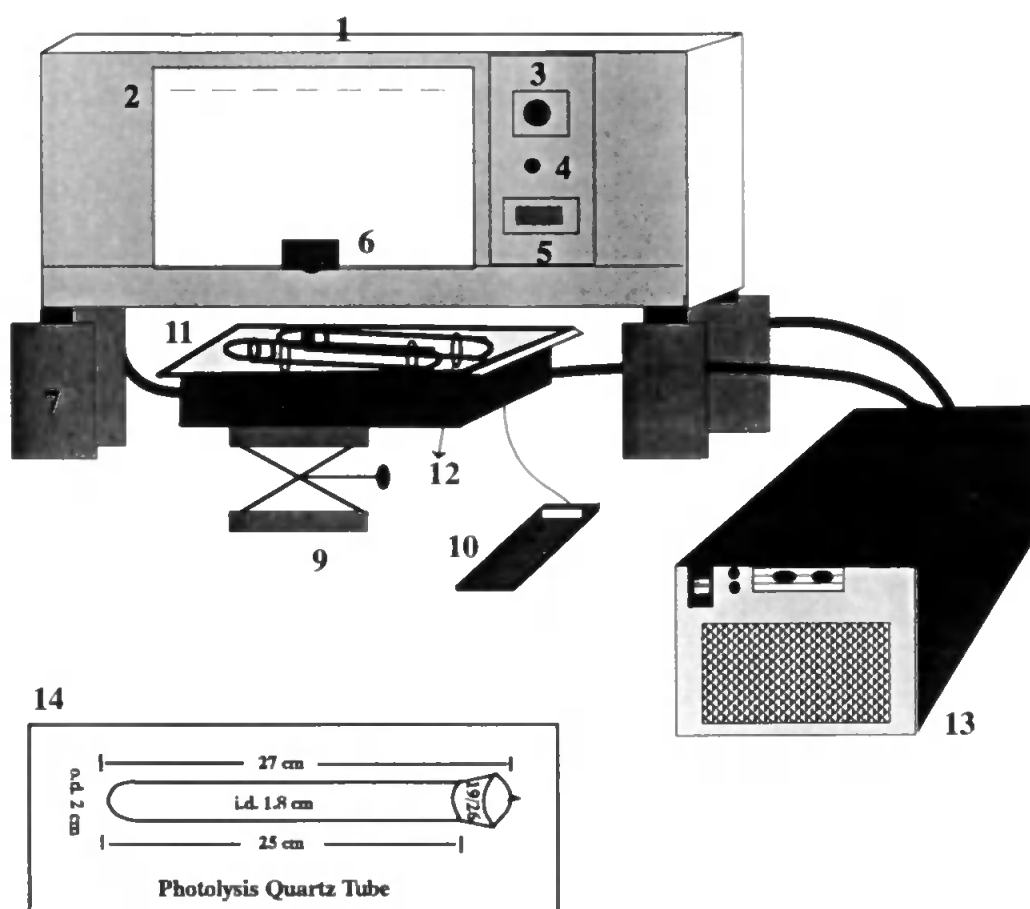


Figure 4.3 Photolysis experimental setup; 1= Heraeus Suntest exposure machine; 2=xenon lamp; 3= lamp potentiometer setting regulator; 4=lamp switch; 5= lamp meter; 6= lamp compartment; 7=wooden block; 8= stainless steel tank; 9= jack to support the tank; 10= thermocouple and thermometer; 11= photolysis quartz tubes; 12=tube holder; 13= chiller unit; 14= profile view of quartz tube showing the dimensions.

thermostated water bath in a dark fume cupboard to adjust the temperature of the solution to 25 °C. The details of the preparation apparatus are shown systematically in **Figure 4.4**.

The sampling was carried out by withdrawing a known volume of the phenanthrene-spiked seawater solution from the reagent flask using a 50 mL glass syringe and the sampling needle and putting it into the irradiation tubes. It was determined that a volume of 30–40 mL would contain a sufficient mass of phenanthrene as a starting material to use for the photodegradation.

The reproducibility of sampling and extraction of phenanthrene was tested with triplicates of 20 mL spiked with 5 µg naphthalene- d_8 internal standard. After analysing by GC, the RSD calculated for the triplicates was 8.8%, showing satisfactory reproducibility.

4.3.3 Method of Exposure

Plate 4.1 shows the xenon lamp and the arrangements made for sample exposure. Radiation was emitted from a 1.8 kW xenon-arc installed horizontally in a parabolic reflector and fitted with a UV filter, the radiation limit at approximately 290 nm in the UV range, corresponding to sunlight. A quartz glass dish with a reflective coating which transmits UV and visible radiation was located below the lamp. The UV and visible components of the xenon radiation emitted vertically were reflected back onto the sample table by the mirror installed above the lamp (**Figure 4.5**).

An arrangement was made so that five solutions in individual stoppered quartz tube could be placed beneath the xenon lamp. Each tube held a maximum of 50 mL. After being

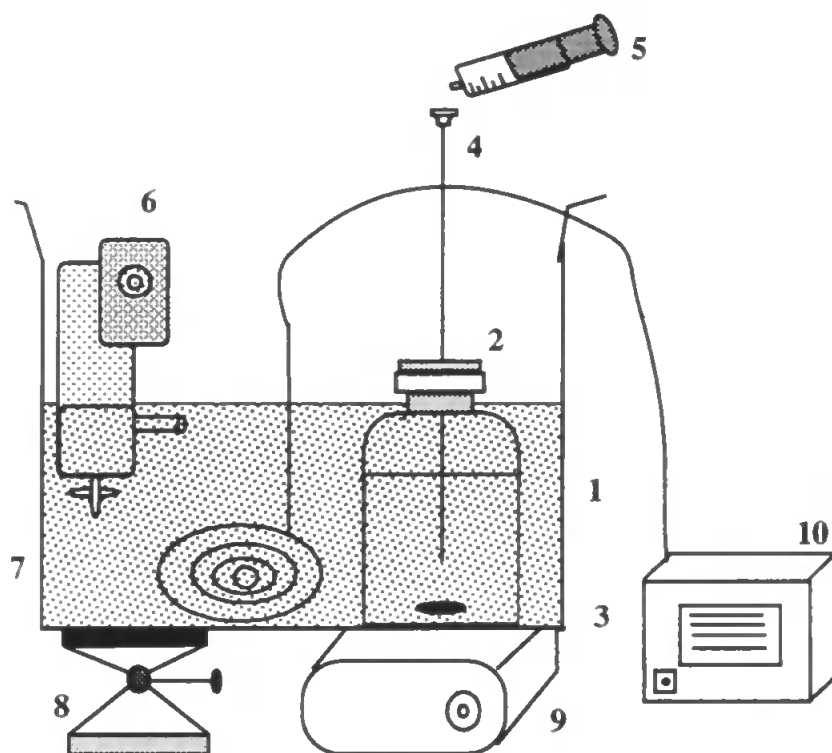


Figure 4.4 The experimental setup for the preparation of phenanthrene in seawater solution for photolysis experiments; 1 = preparation flask; 2 = Suba.Seal; 3 = magnetic stirrer; 4 = sampling needle; 5 = glass syringe; 6 = thermostirrer; 7 = thermostated waterbath; 8 = lab jack; 9 = stirring block; 10 = chiller unit.



Plate 4.1 The xenon lamp and the arrangements made for sample exposure.

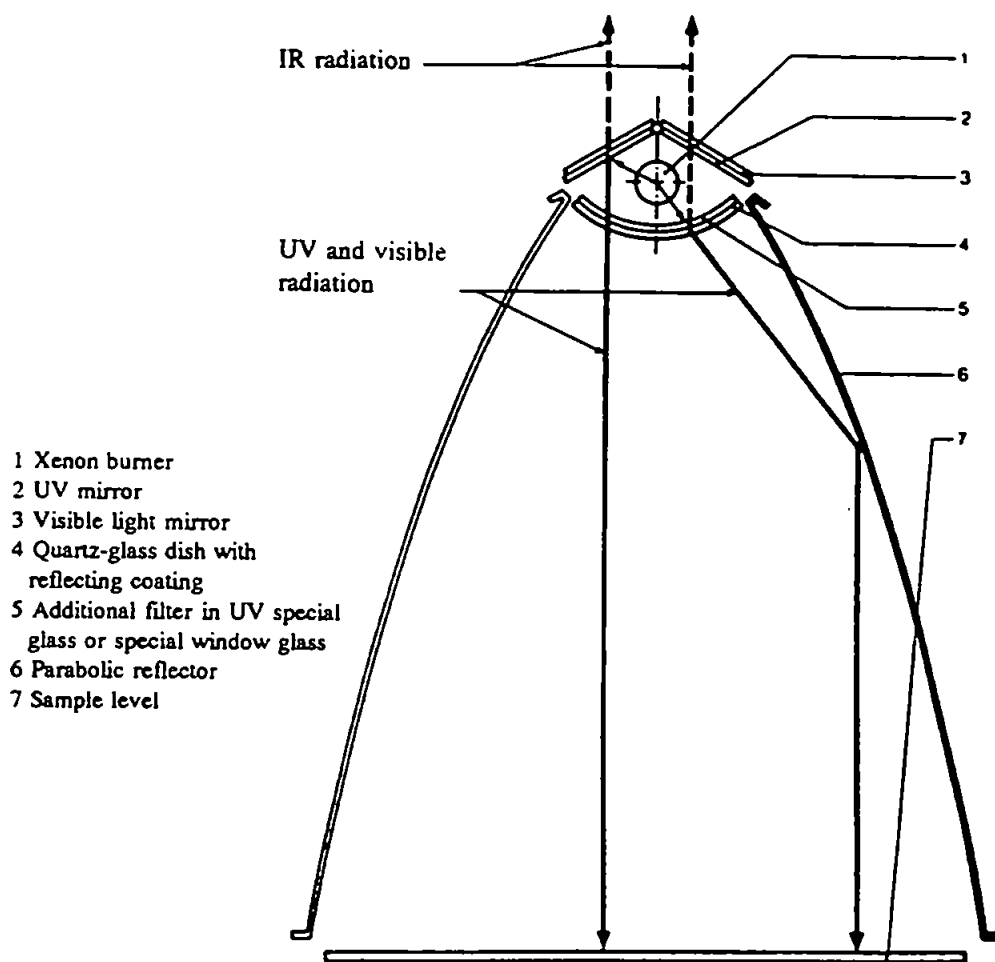


Figure 4.5 Xenon lamp as installed inside the Suntest CPS instrument (Heraeus GmbH operating manual).

filled with the phenanthrene solution, they were tightly capped and a piece of PTFE tape was added to keep the stopper and tube tightly sealed. This minimised any volatilisation that may occur during irradiation.

To maintain a constant temperature during irradiation, the tubes were held in a specially designed stainless steel tank (Parker and Leahey, 1988) partially filled with glycerol, in a metal holder. The tank was cooled by circulating thermostated water through the tank. Glycerol was used instead of water to avoid loss of coolant due to evaporation. The tank holding the tubes was positioned under the light source (the tank replaces the sample table in the unit) with the aid of a laboratory jack at a distance of approximately 20 cm from the lamp (see **Figure 4.3**). The temperature of the glycerol during irradiation was monitored using 5 thermocouples fixed at different locations in the tank and read by a digital thermometer.

Before sample irradiation, the lamp and the cooling of the glycerol tank were switched on for an hour to allow the lamp to reach its maximum radiation intensity and for the glycerol to adjust to the temperature required. When the irradiation time of a sample was completed, the tank was promptly lowered and the tube was carefully slid out of the holder and replaced by another sample as required.

Measurements of the Radiation Intensity

The radiation intensity of the xenon lamp incident on the reaction tubes was measured at seven different locations on the sample trays as shown in **Figure 4.6**, using a UDT 81 Optometer with a broad band filter which integrated total energy between 400-1000 nm. These measurements were made to find out if the radiation was uniformly received across

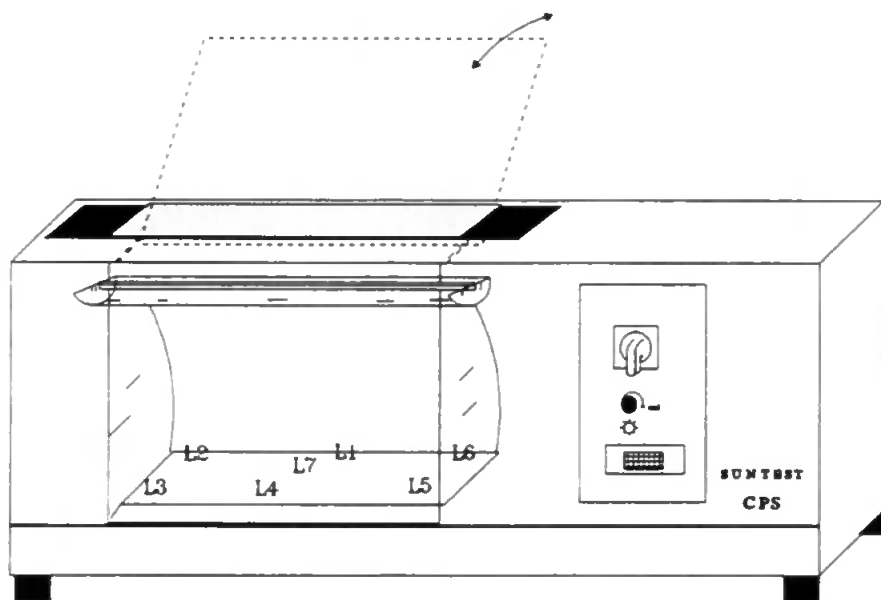


Figure 4.6 Cross section view of xenon lamp compartment showing the location of the radiation intensity measurements taken under the lamp (see Table 4.3).

the bed of the glycerol tank holding the reaction tubes under the lamp. The radiation intensity of the lamp was also measured at all the radiation intensity settings of the instrument, rating from maximum setting (cal) to the lowest setting (1). All these measurements were recorded and are presented in Table 4.3.

The results showed that there is a linear relationship between increasing the lamp potentiometer setting and radiation intensity for each location measured under the lamp as graphically presented in Figure 4.7. Also the decrease in radiation intensity increases as one goes from an additional point down the scale of the potentiometer. These measurements are particularly useful when investigating the effect of radiation intensity on the degradation of a substrate by varying the intensity setting of the lamp. The data did show that for any one setting (i.e. 1,2,3, cal), the radiation intensity varied with location. For example, the calculated RSD for (cal) setting was 1.19 % (Table 4.3) for locations between L1 to L7. However as this variation is < 5% (and similarly for the other settings), it could be taken within the experimental error that the radiation across the bed of the sample bath was fairly constant. Therefore the mean value can be used as a measure of the radiation intensity incident on the sample surface under the lamp.

The quartz tubes were subjected to an average radiation intensity of 194 W/m² from the maximum radiation setting (cal) of the lamp. A control sample (triplicate or duplicate) and seawater blanks were included in each experiment. At the end of the exposure time the tubes were removed from the bath and left to cool in a refrigerator before opening for workup.

Table 4.3 Measurement of the radiation intensity of the xenon lamp.

Xenon lamp Potentiometer Setting	Radiation intensity W m ⁻²									
	L1 ^a	L2 ^a	L3 ^a	L4 ^a	L5 ^a	L6 ^a	L7 ^a	Mean	S.D. _(n-1)	R.S.D
cal	197.0	197.3	194.6	192.0	192.6	193	191.8	194.0	2.31	1.19
7	194.8	195.7	192.1	189.6	191.2	192.8	191.8	192.6	2.10	1.09
6	189.0	191.3	187.3	184.7	186.1	187.6	184.4	187.2	2.43	1.30
5	184.1	185.4	181.8	178.5	180.3	181.5	178.3	181.4	2.69	1.48
4	176.1	177.6	173.2	170.4	171.6	173.5	169.6	173.1	2.92	1.69
3	166.7	168.5	164.6	162.1	162.3	164.0	159.5	163.9	3.02	1.84
2	149.6	158.7	154	150.7	154.5	155.2	150.3	153.3	3.27	2.13
1	145.5	146.5	144.8	141.0	141.0	142.3	140.0	143.0	2.56	1.79

^a Location of measurement under the lamp, see Figure 4.6

Lamp was run for 48 hr before taken measurements.

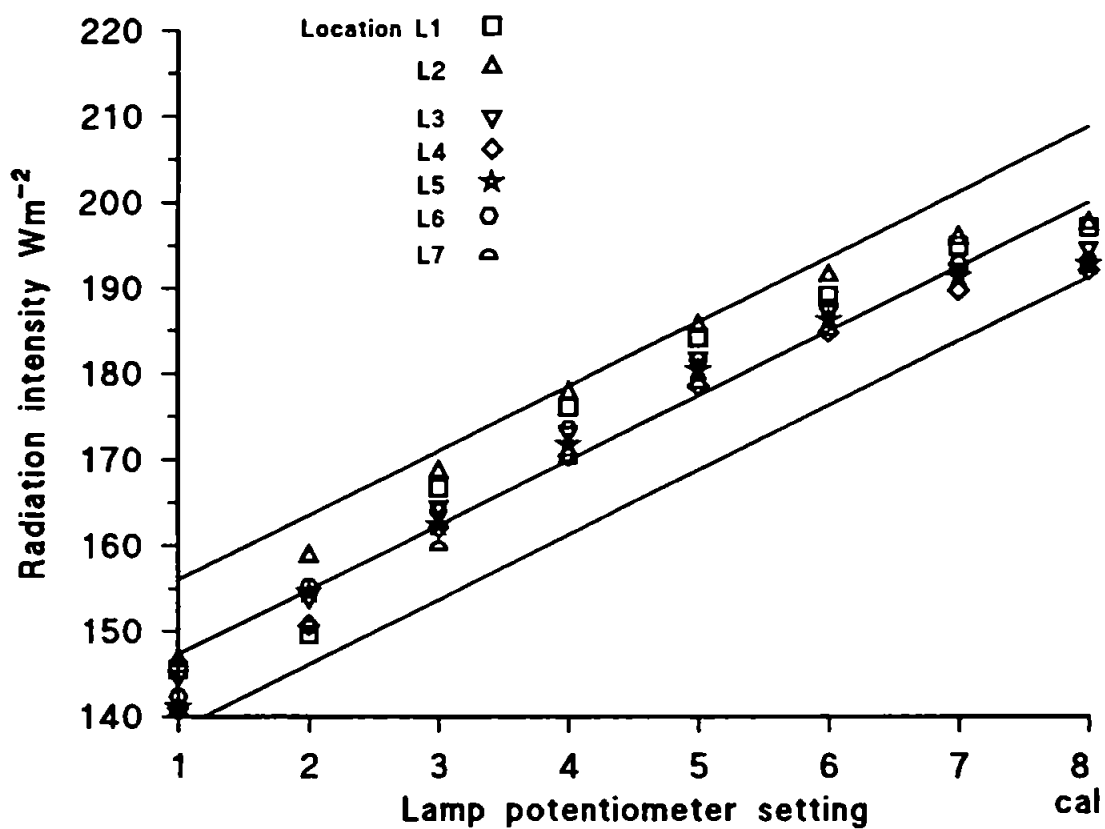


Figure 4.7 The relationship between xenon lamp potentiometer setting and the amount of radiation at different locations (L1-L7) under the lamp, see also Table 4.3.

4.3.4 Workup of Irradiated Phenanthrene Solution

After allowing the irradiated samples to cool, the tubes were opened and the samples spiked with an internal standard. Two separate standards were used for the irradiated samples: deuterated naphthalene (10 μg) was used in experiment 1 and 2, and 3-methylphenanthrene (10 μg) was used in experiment 3 and 4. This amount of internal standard was determined after trial mixing and extraction experiments using different relative amounts of naphthalene- d_8 (5, 10, 15 or 20 μg) or 3-methylphenanthrene (5, 10, 15 or 20 μg) to phenanthrene (24 μg).

The spiked samples were then carefully decanted from the quartz tubes into separating funnels, the tubes were rinsed with 5 mL of pentane which was added to the separating funnel and shaken. After phase separation, the pentane fraction was collected. The above extraction procedure was repeated with a further 5 mL of pentane and the pentane extracts were stored in sealed vials. The extracts were dried by passing through an anhydrous sodium sulphate micro-column.

The extracted samples were concentrated using a controlled micro Kuderna-Danish concentrator and finally with a very gentle stream of N_2 to 0.5 mL as described in chapter 4 and analyzed by GC or GC-MS (see below). Throughout the sample preparation procedure, extreme care was taken to ensure that exactly the same treatment was applied to all samples so as to eliminate any variation in the results.

To identify the photodegradation products, the pentane extracts were examined by GC-MS. The aqueous phase of the control and selected irradiated samples were also examined after

acidification and methylation by two methods: the first was methylation with BF_3 -methanol reagent; the second was with CH_3I according to Gillis (1968).

4.3.5 Methods of Analysis

GC Analysis

Gas chromatography analyses used in experiment 1 and 2 were performed using a Carlo Erba Mega Gas Chromatograph fitted with an FID and on-column injection. The oven was equipped with a 30 m x 0.32 mm i.d. (0.25 μm film thickness) DB-5 fused silica capillary column (J&W, U.K). The oven was programmed from 40 °C to 300 °C at 10 °C min^{-1} + 10 min hold at 300 °C. Carrier gas was hydrogen at 2 mL min^{-1} . Peak areas were integrated with a Shimadzu-CR3A integrator.

GC-MS Analysis

Gas chromatography-mass spectrometry analyses used in experiment 3 and 4 were performed using a Hewlett Packard MSD fitted with a 12 m x 0.2 mm (0.33 μm film thickness) HP-1 fused silica capillary column (Hewlett Packard, U.K). The oven was programmed from 40 °C to 300 °C at 6 °C min^{-1} . Carrier gas was helium at 2 mL min^{-1} . Injection temperature was 250 °C and injection (1-2 μL) was made automatically in the splitless mode. Helium was used as the carrier gas. Electron impact spectra were obtained at 70 eV, 1.2 scans sec^{-1} and mass range of 50-500 Daltons.

Identification of phenanthrene photodegradation products was made by comparison of mass spectra reported in the literature (Dowty *et al.*, 1974; Patel *et al.*, 1978) and confirmed by coinjection with authentic compounds when available. A solution containing

phenanthrene and the authentic identified photodegradation products was analysed and the retention time relative to phenanthrene was measured and compared with the relative retention times of the products in the irradiated samples to confirm the identification. The quantification was made with reference to 3-methylphenanthrene internal standard.

The relative response factor (RRF) between phenanthrene and the naphthalene- d_8 internal standard used in experiment 1 and 2 was determined by analysing equal amounts of the two compounds (IOC/UNESCO, 1982) and the concentrations were corrected accordingly.

UVF Analysis

UVF analyses used in experiment 4 were made using a Perkin Elmer MPF-3 ultraviolet fluorescence spectrophotometer after the method of Østgaard and Jensen (1983b). Calibration was made with phenanthrene standard solutions in seawater. A standard solution of $10\ \mu\text{g mL}^{-1}$ of phenanthrene in acetone was first prepared and then an aliquot was added to seawater to prepare solutions between $0\text{--}1\ \mu\text{g mL}^{-1}$.

The solutions were excited at 230 nm and the emissions were recorded between 200–800 nm. The excitation and emission slit-width were 15 nm and 5 nm, respectively. The emission spectra showed distinctive peaks at 348 nm, 365 nm and 385 nm. A calibration curve was constructed from the fluorescence intensity of the phenanthrene standard solutions measured at 348 nm (the wavelength showing highest emission). The fluorescence intensity of the irradiated and non-irradiated samples were all measured at the same wavelengths (i.e. 230 nm excitation; 348 nm emission) and the concentrations were obtained from the calibration curve.

The irradiated and non-irradiated phenanthrene samples were also examined by synchronous scanning emission directly in the water phase for the products. Authentic compounds of the identified photodegradation products were prepared individually in a polar solvent (ethanol) at an equimolar concentration of 1.12×10^{-5} M (standards were first dissolved in acetone). The maximum excitation wavelengths for individual compounds were determined and used to obtain the emission wavelengths of each compound.

4.3.6 Photodegradation Experiment 1

A first attempt was made to establish the photodegradability of phenanthrene under the constructed irradiation system, and to investigate the factors that could affect the degradation. For this, the phenanthrene samples (30 mL) were irradiated for 3, 6, 12, 24 and 48 hours. Control samples were analysed in triplicate. The thermostatic tank was cooled in this initial experiment using flowing tap water and at the start of irradiation the temperature was 15 °C. After irradiation, the samples were prepared and analysed by GC.

The RRF between phenanthrene and naphthalene- d_8 was found to be 1.3 ($n=5$, RSD 9%), thus all concentrations of phenanthrene as a function of irradiation time were corrected accordingly as presented in Table 4.4.

The concentration of the triplicate samples of phenanthrene determined by GC at 0 hr irradiation showed a satisfactory reproducibility (RSD 8.5%) especially given that workup entailed several preparation processes (i.e. sampling, extraction, K-D concentration and analysis). The photodegradation of phenanthrene as obtained from this experiment is illustrated in Figure 4.8. A rapid decrease in the concentration was observed, relative to

Table 4.4 Photodegradation of phenanthrene irradiated under xenon lamp as obtained from experiment (1) by GC.

Irradiation Time (hr)	Temperature of Sample (°C)	Concentration $\mu\text{g mL}^{-1}$	Concentration Relative to 0 hr (%)
0	15	1.04	100 ^a
0	15	0.88	100 ^a
0	15	1.00	100 ^a
3	36.2	0.04	4
6	37.1	0.03	3
12	41.4	0.00	0
24	42.2	0.00	0
48	43.3	0.00	0

^a Mean of the triplicate = $0.973 \mu\text{g mL}^{-1}$ (100 %); RSD = 8.5 %

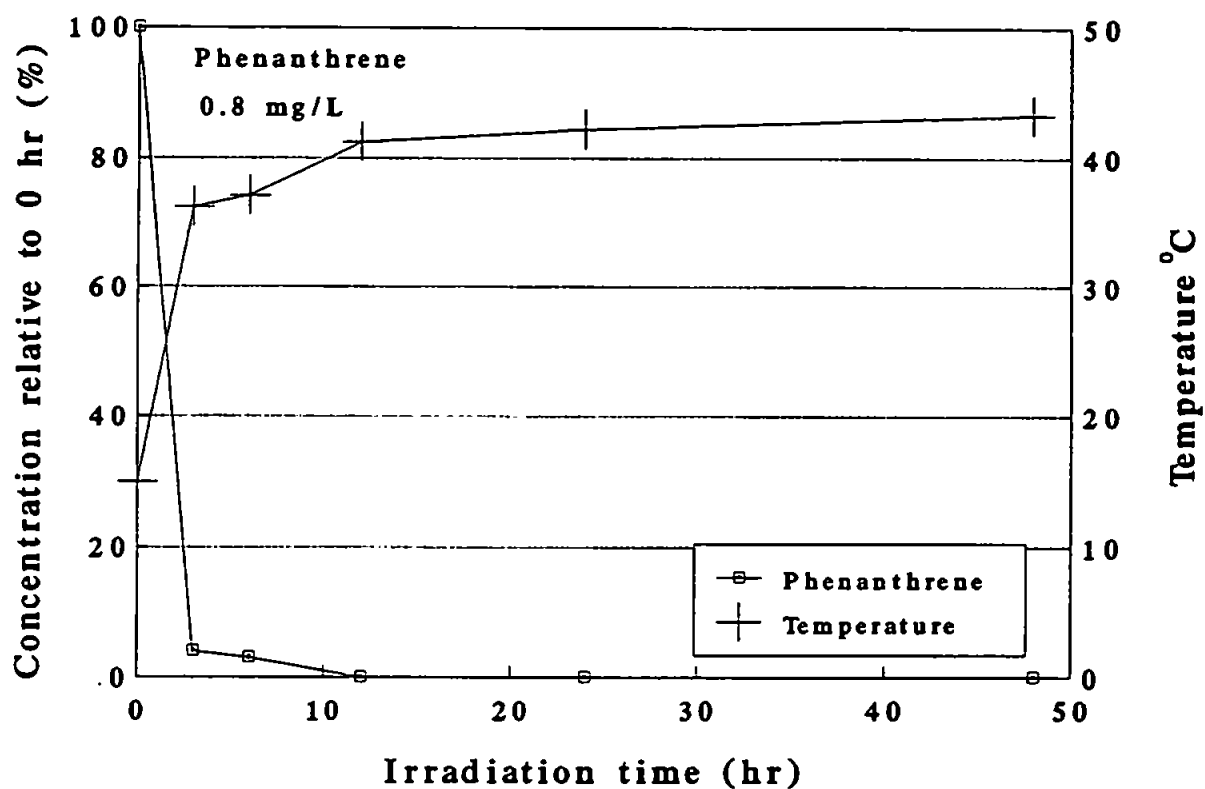


Figure 4.8 Photodegradation of phenanthrene in seawater irradiated under xenon lamp for specified times as obtained from experiment 1 and determined by GC-MS.

concentration at 0 hr, from 100% to 4% between 0-3 hours of irradiation and reaching 0 at 12 hours. The sharp decrease in the concentration after less than 3 hours of irradiation was interesting for two reasons. It showed that either phenanthrene was largely photodegraded within 3 hours, or that, the rapid degradation was due to the rise in the sample temperature (temperature increased from 15 °C to 36 °C in 3 hr and continued to rise to ≈ 43 °C at the end of experiment) caused by heat from the lamp during irradiation (Figure 4.8). As pointed out by Zepp (1982) xenon lamps produce a lot of heat during operation and require a good cooling system. Therefore it is possible that the increase in temperature accelerated the photodegradation rate constant (k_p) as expected from the Arrhenius equation (see Section 4.1.1).

To examine the effect of controlling the temperature on the photodegradation of phenanthrene, a second experiment was carried out to improve the irradiation conditions, particularly controlling the sample temperature during irradiation and to focus on shorter irradiation times.

4.3.7 Photodegradation Experiment 2

Experiment 1 indicated that flowing tap water could not maintain a stable sample temperature during irradiation, so a small chilling unit was used to circulate cooled water (< 10 °C) around the glycerol tank holding the tubes. Also, it was seen from experiment 1 that phenanthrene degraded in less than 6 hours, so phenanthrene samples were irradiated for 0.5, 1, 2, 3 and a maximum of 6 hours.

The results obtained from this experiment are presented in Table 4.5 and Figure 4.9. The

Table 4.5 Photodegradation of phenanthrene irradiated under xenon lamp as obtained from experiment (2) by GC.

Irradiation Time (hr)	Temperature of Sample (°C)	Concentration $\mu\text{g mL}^{-1}$	Concentration Relative to 0 hr (%)
0	18.8	1.09	100 ^a
0	18.8	1.50	100 ^a
0.5	27.7	1.06	81.5
1.0	31.1	1.0	77
2.0	29.1	0.65	50
3.0	28.5	0.63	48.5
6.0	26.5	0.33	25

^a Mean of the duplicate = $1.3 \mu\text{g mL}^{-1}$ (100 %)

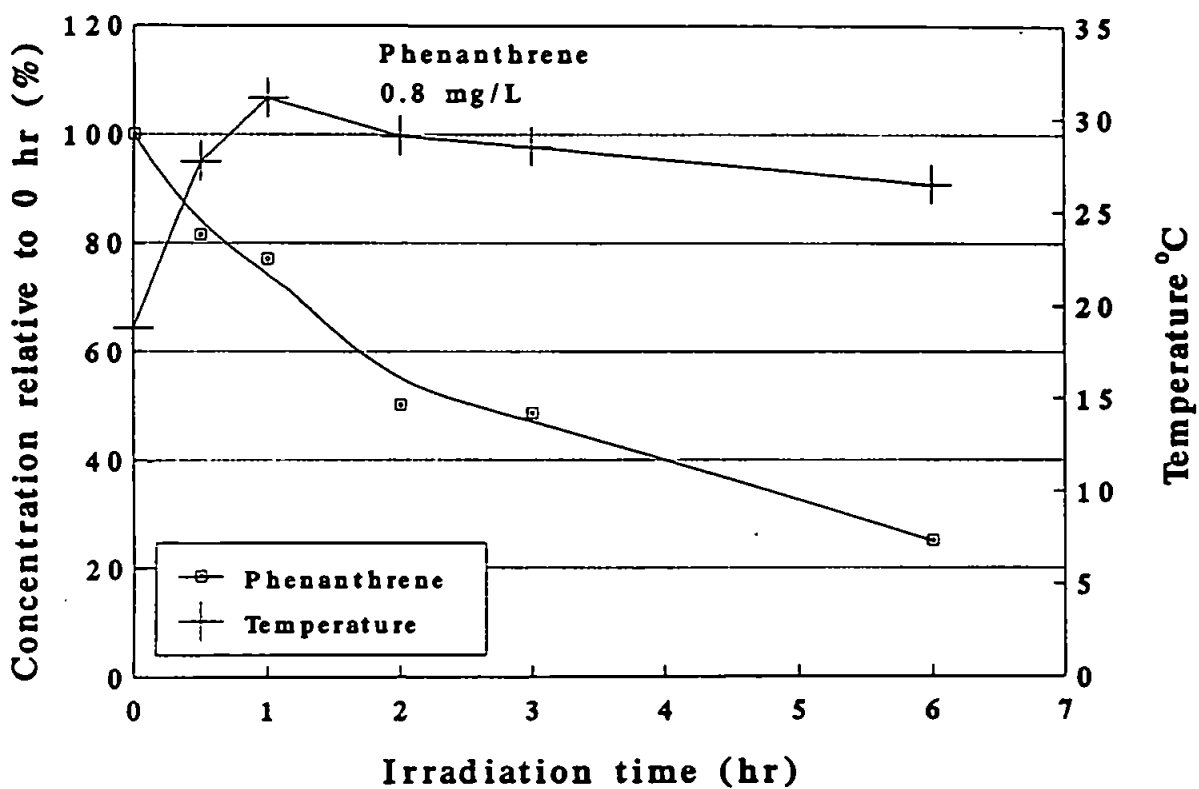


Figure 4.9 Photodegradation of phenanthrene in seawater irradiated under xenon lamp for specified times as obtained from experiment 2 and determined by GC-MS.

decrease in the concentration of phenanthrene determined by GC was not as rapid as in experiment 1. The concentration relative to phenanthrene at 0 hr decreased from 100% to 50 % after 2 hours of irradiation. A slower degradation proceeded thereafter where a further 25% decrease occurred after 4 hours of irradiation. The effect of controlling the temperature on the photodegradation of phenanthrene was therefore obvious compared to results obtained from experiment 1. Miller and Zepp (1983) mentioned that an increase in sample temperature can increase the rate of photolysis as demonstrated in studies of pesticides. During this experiment, the temperature varied between 19 °C and 31 °C. However this variation, although less than in experiment 1, has still caused the irregularity in the photodegradation as shown in **Figure 4.9**.

Therefore, it was concluded that to obtain a more reproducible photodegradation and to provide kinetic data, the experiment should be isothermal during the entire irradiation period. Hence, a third experiment was carried out at 25 °C (i.e. average summer water temperature of the Arabian Gulf, al-Abdul-Razzak, 1984).

4.3.8 Photodegradation Experiment 3

A high power chilling unit with a cooling capacity of 700 W at 0 °C (see also **Appendix 3**) was purchased and employed to maintain the temperature at 25 °C during irradiation. Before starting to irradiate samples, the temperature of the glycerol was examined at the location of each tube in the tank while the lamp and chiller unit was operating. The temperature recorded varied between 22 °C to 25 °C due to variation in the tank geometry. It was found that the tubes closest to the incoming water were at a lower temperature than the tubes closest to the outlet. However, this temperature variation was small and was

maintained over the long irradiation periods. Having regulated the temperature, samples were irradiated for 1,2,3 and 4 hours and prepared for analysis by GC-MS.

Derivatisation of the Aqueous Phase of Phenanthrene After Pentane Extraction

To identify any photodegradation products, the aqueous hyperphase, which may be expected to contain any acidic photoproducts after pentane extraction, was acidified with concentrated HCl (to pH 2) then extracted with DCM. The extracts were reduced to a minimum volume with a micro K-D and derivatised with BF₃/methanol. This was achieved by boiling the extract with 5 mL of the derivatising complex. Distilled water (50 mL) was then added to destroy the excess reagent. The samples were finally extracted with DCM, reconcentrated by K-D and analysed by GC-MS. The pentane extracts were also examined by GC-MS for photodegradation products.

Photodegradation Kinetics of Phenanthrene as Determined from Experiment 3

The results of the GC-MS analysis of irradiated and non-irradiated phenanthrene samples are presented in Table 4.6 and Figure 4.10. The phenanthrene concentration showed a steadier decline with increasing time of irradiation after controlling the sample temperature at 22-25 °C (Figure 4.10). The phenanthrene concentration decreased from 100% to 51% (49% degradation) relative to concentration at 0 hr after 2 hours of irradiation. A slower degradation was shown thereafter at which 25% photodegradation took place after a further 2 hours. Figure 4.10 showed that the concentration of phenanthrene decreased exponentially with time i.e.,

$$C_t = C_0 e^{-k_p \cdot t}$$

where C_t is the concentration at time t ; C_0 is the initial concentration. Therefore phenanthrene photodegradation may be described as a pseudo first-order reaction i.e.,

Table 4.6 Photodegradation of phenanthrene irradiated under xenon lamp as obtained from experiment (3) by GC-MS.

Irradiation Time (hr)	Temperature of Sample (°C)	Concentration $\mu\text{g mL}^{-1}$	Concentration Relative to 0 hr (%)	Degradation (%)
0	24.9	0.82	100 ^a	0
0	24.9	0.89	100 ^a	0
1	22.4	0.62	72	28
2	25.5	0.44	51.2	49
3	25.8	0.31	36	64
4	24.5	0.22	25.6	74.4

^a Mean of the duplicate = $0.86 \mu\text{g mL}^{-1}$ (100 %)

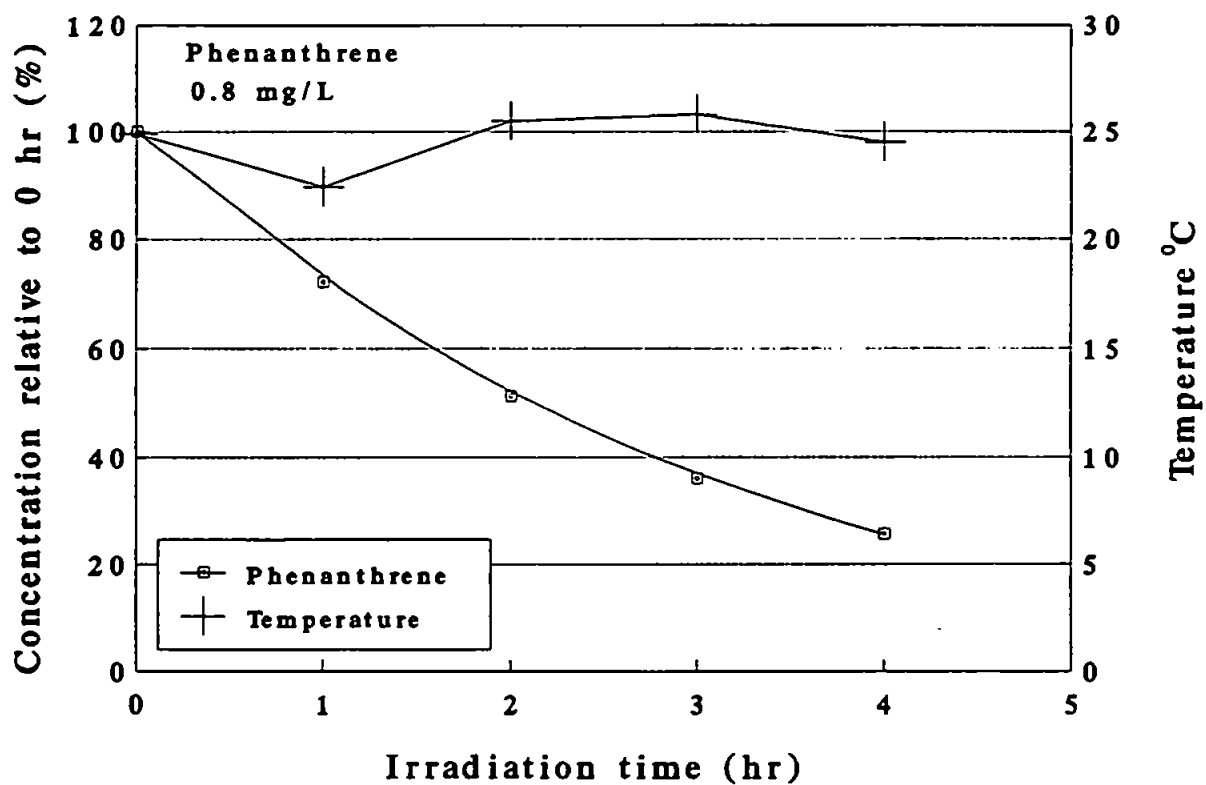


Figure 4.10 Photodegradation of phenanthrene in seawater irradiated under xenon lamp for specified times as obtained from experiment 3 and determined by GC-MS.

$$\ln [C_t/C_0] = -k_p t$$

The values of $\ln [C_t/C_0]$ were calculated and plotted against time of irradiation. A good fit of regression line was obtained with correlation coefficient $r = 0.9999$. The value of the photodegradation pseudo first-order rate constant (k_p) of phenanthrene was the slope of the graph shown in **Figure 4.11** which was $-0.342 \text{ hr}^{-1} \pm 0.0025$ at 99.5% confidence limits. Thus, the half-life of phenanthrene:

$$\begin{aligned} t_{1/2} &= 0.693 / k_p \\ &= 2.03 \text{ hr.} \end{aligned}$$

Photodegradation Products of Phenanthrene

Examination of the DCM extract by GC-MS after derivatisation with BF₃/methanol did not reveal any photodegradation products. Examination of the pentane extract of the irradiated phenanthrene compared to the control and seawater blank indicated some photodegradation products at very low concentrations. The products identified in the order of abundance after four hours irradiation were: 3,4-benzocoumarin (4 ng mL⁻¹), fluorenone (1.2 ng mL⁻¹), and 2,3:4,5-dibenzoxepin (0.24 ng mL⁻¹) (**Figure 4.12**). In general, the concentration of these products increased with increasing time of irradiation of phenanthrene under the xenon lamp. However, after 4 hours of irradiation, 74.4% of the phenanthrene had been degraded of which only 0.72 % was identified as photodegradation products.

4.3.9 Summary of Experiments 1 to 3

Control of the sample temperature during irradiation removed one of the major variations affecting the photodegradation of phenanthrene with two consequences. Firstly, the

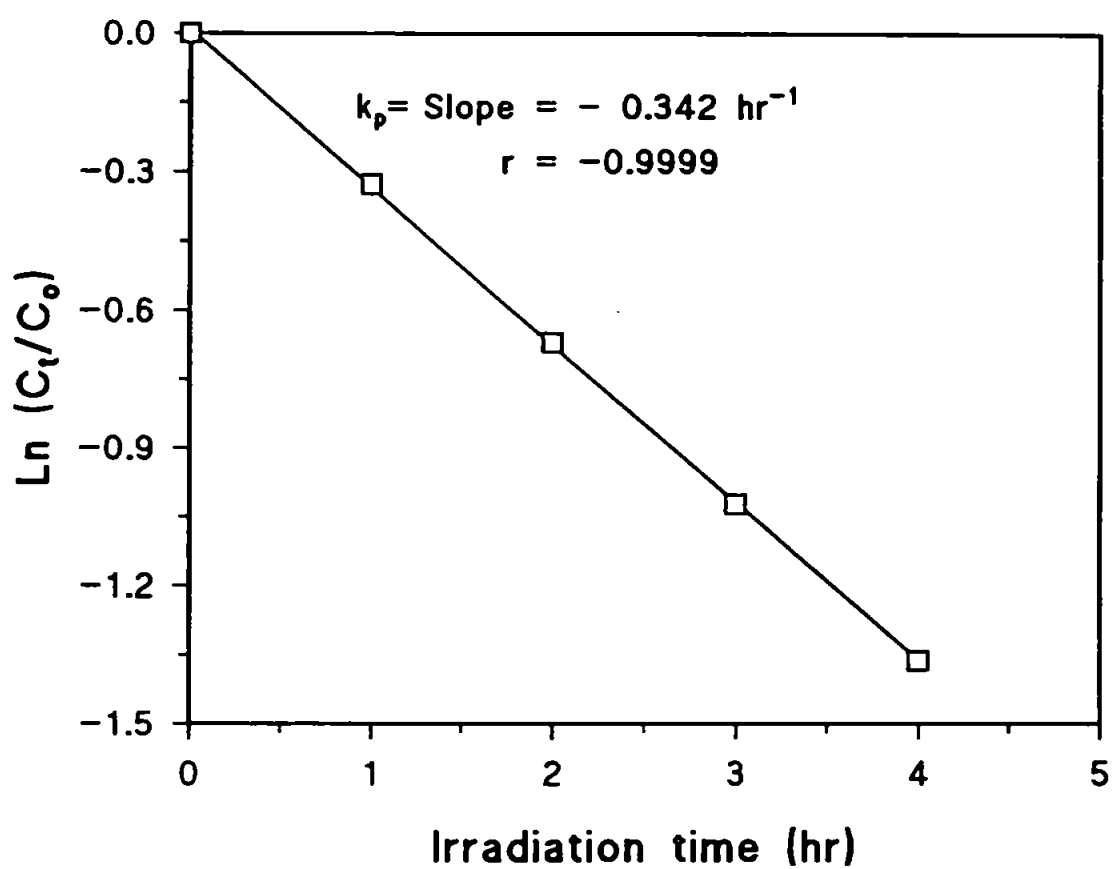


Figure 4.11 Photodegradation rate constant (k_p) of phenanthrene as obtained from experiment 3 and determined by GC-MS.

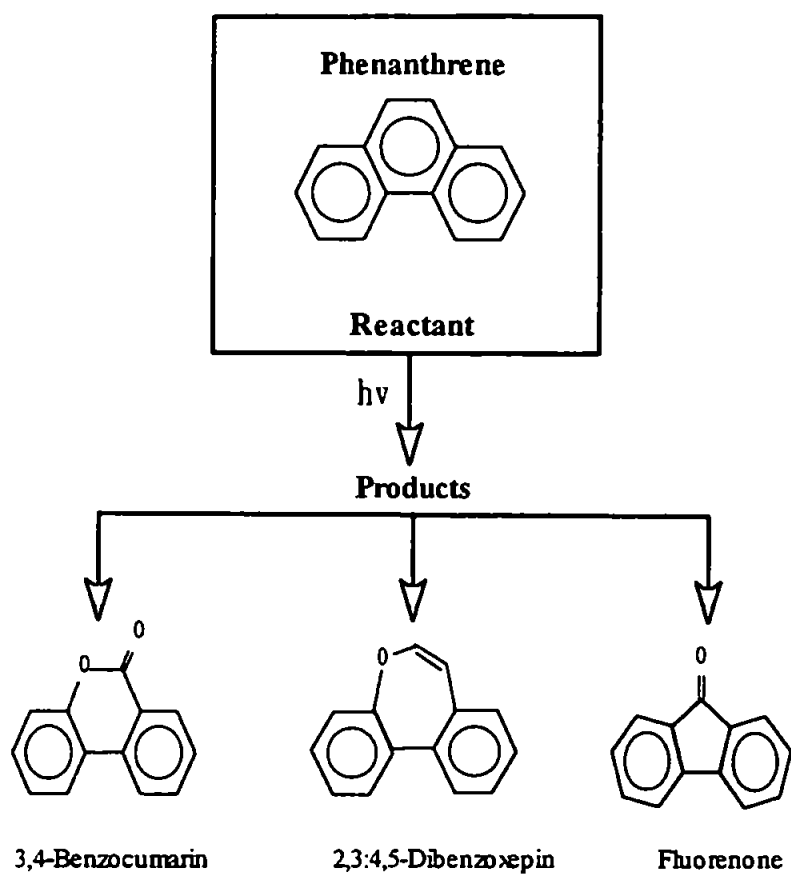


Figure 4.12 Products formed during photodegradation of phenanthrene under xenon lamp in experiment 3.

photodegradation was found to decrease systematically as described by a pseudo first-order reaction and a half life of 2.03 hr at 25 °C in the presence of 194 Wm⁻² light intensity. Secondly, some photoproducts were detected. However, the photodegradation products which were identified accounted for only a small percentage of the total phenanthrene photodegraded.

To examine the reproducibility of these results, and to demonstrate that the detection of the acidic oxygenated products, which may have formed upon irradiation of phenanthrene, was independent of the derivatisation methodology, a fourth experiment was made in which another derivatisation method (Gillis, 1968) was used.

4.3.10 Photodegradation Experiment 4

The optimised photodegradation method achieved from experiment 3 was repeated in experiment 4 to irradiate samples of phenanthrene for 1,2,4,6 and 7 hours. The experimental design for the irradiation and preparation of phenanthrene samples is shown in **Figure 4.13**. After irradiation, an aliquot (10 mL) of each irradiation solution, the control and seawater blanks examined by UVF directly of the aqueous phase. The remaining 30 mL portion of the irradiated phenanthrene solutions were extracted with pentane and prepared for GC-MS analysis as shown in **Figure 4.13**.

The aqueous hyperphases remaining after pentane extraction were further extracted twice. Firstly with DCM after adding 5 µg of 3-methylphenanthrene as an internal standard. Secondly, the aqueous hypophase after DCM extraction was acidified with concentrated HCl (to pH 2) and again extracted with DCM (50 mL) in a continuous liquid/liquid

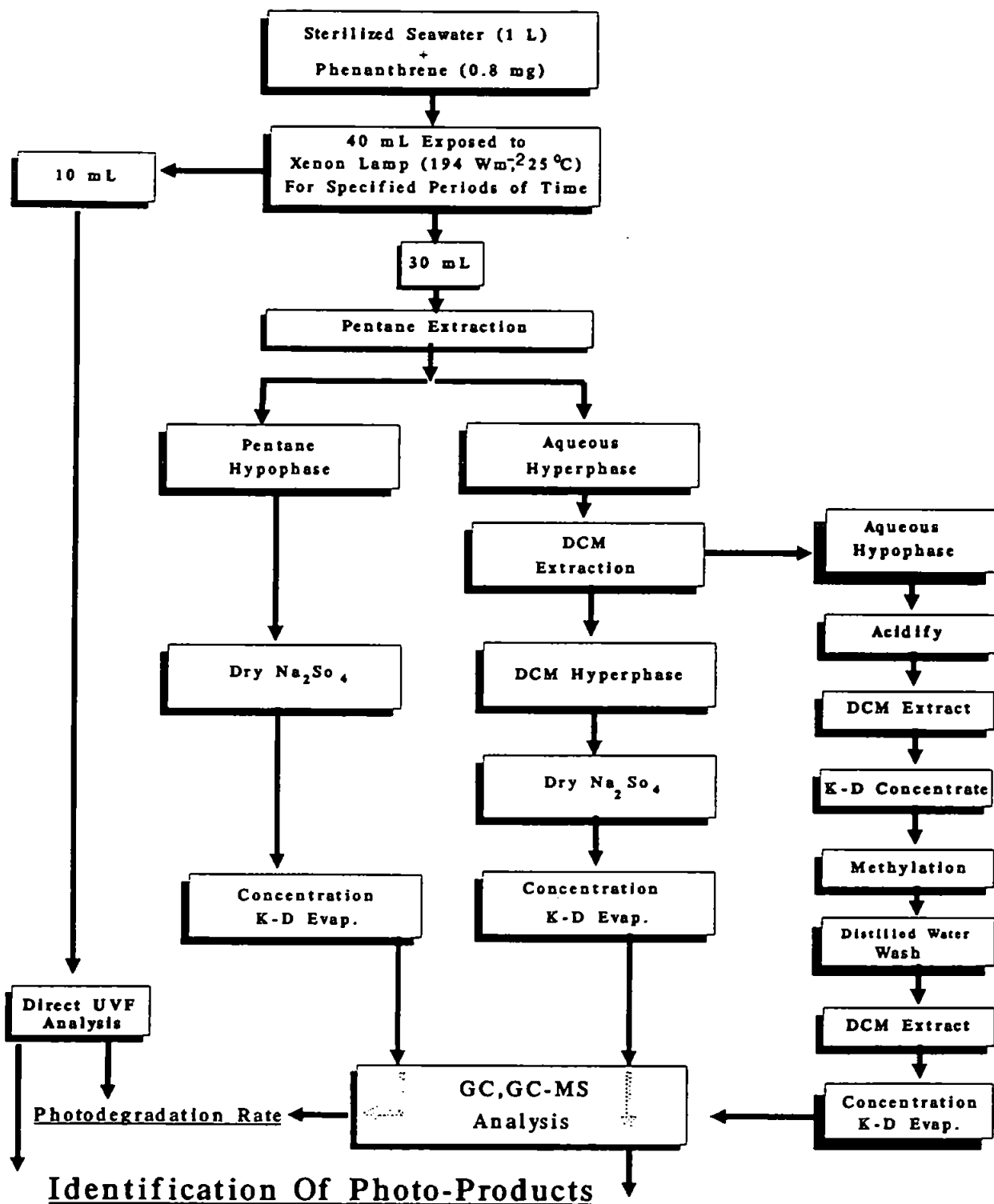


Figure 4.13 The experimental design for the irradiation and preparation of phenanthrene samples.

extraction apparatus for three days to increase the extraction efficiency. The extracts were then methylated using methyl iodide and sodium hydroxide in dimethyl sulphoxide (CH_3SOCH_3) according to the method of Gillis (1968).

All prepared extracts were analysed by GC-MS as described earlier (Section 4.3.5). The injection volume on GC-MS was increased to 2 μL in order to increase the limit of detection of the photo-products.

4.4 Results and Discussion

4.4.1 Photodegradation Kinetics of Phenanthrene

The photodegradation of phenanthrene achieved from this experiment is shown in **Figure 4.14**. About 45% photodegradation occurred after 2 hr and 91% after 7 hr of irradiation (**Table 4.7**). The photodegradation rate constant obtained from this experiment from the pseudo first-order linear regression was $-0.317 \pm 0.029 \text{ hr}^{-1}$ at 99.5% confidence limits (**Figure 4.15**). The half-life calculated was 2.19 hr.

Comparison of the GC-MS results for phenanthrene photodegradation from this experiment with the previous experiment (i.e. experiment 3) showed that the reproducibility was very good ($\pm 0.1 \mu\text{g mL}^{-1}$) which demonstrated that the experiments were carefully performed (**Table 4.8**). The reproducibility was confirmed by the half-life of phenanthrene calculated from experiments 3 (i.e. 2.03 hr) and experiment 4 (i.e. 2.19 hr) under the irradiation conditions used.

Fukuda *et al.* (1988) reported a photodegradation rate constant and half life for

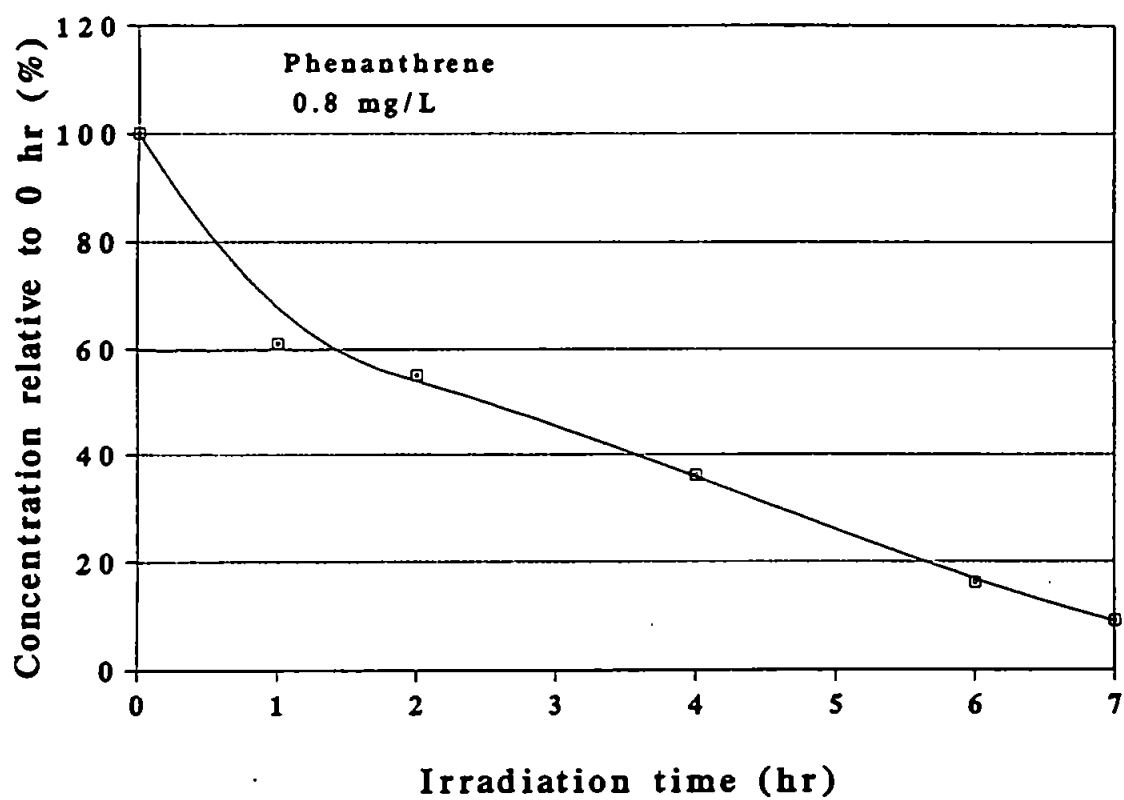


Figure 4.14 Photodegradation of phenanthrene in seawater after irradiation under xenon lamp as obtained from experiment 4 and determined by GC-MS.

Table 4.7 Photodegradation of phenanthrene with time obtained from experiment (4) as determined by GC-MS.

Sample	Concentration $\mu\text{g mL}^{-1}$	Remaining (%)	Degradation (%)
0 hr	0.77	100	0.0
1 hr	0.47	61	39
2 hr	0.42	55	45
4 hr	0.28	36	64
6 hr	0.12	16	84
7 hr	0.07	9	91

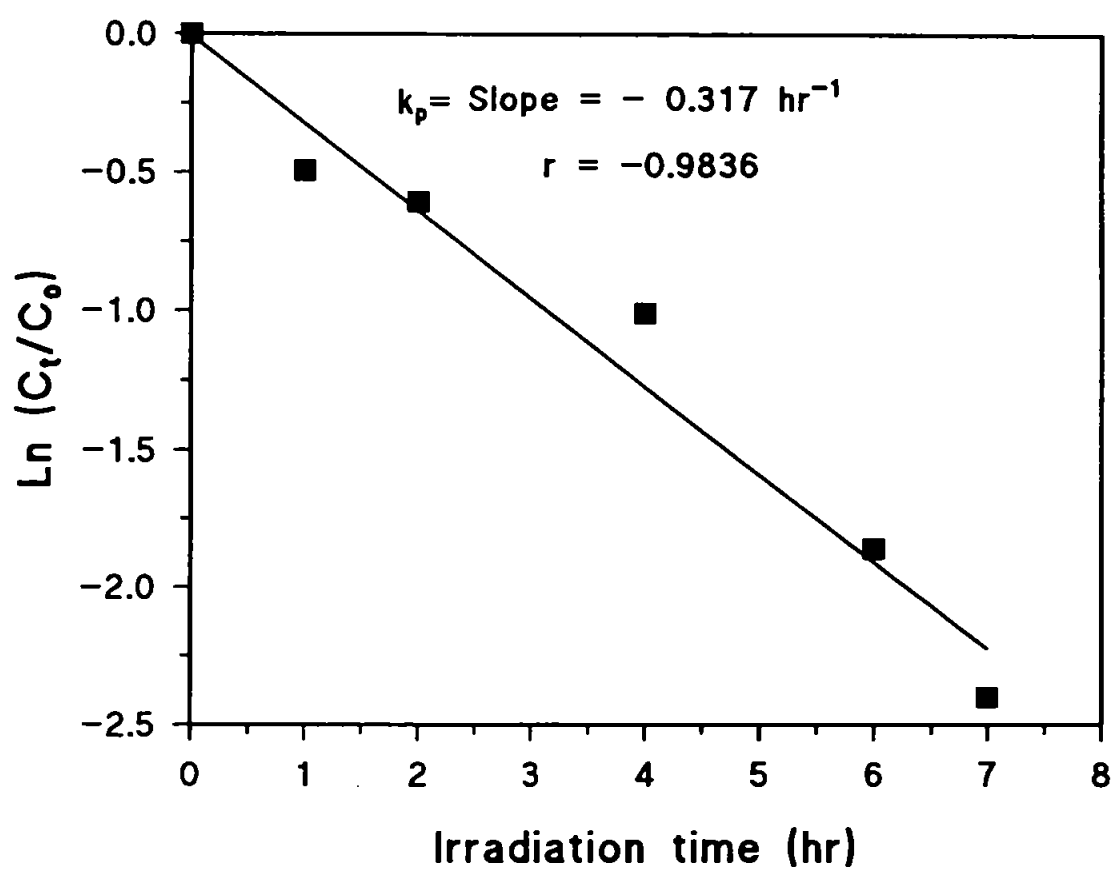


Figure 4.15 Photodegradation rate constant (k_p) of phenanthrene as obtained from experiment 4 and determined by GC-MS.

Table 4.8 Reproducibility between experiment (3) and (4) for phenanthrene photodegradation as determined by GC-MS.

Sample	Concentration $\mu\text{g mL}^{-1}$	
	Experiment 3	Experiment 4
0 hr	0.74	0.77
1 hr	0.59	0.47
2 hr	0.42	0.42
3 hr	0.30	n.d.
4 hr	0.23	0.28
6 hr	n.d.	0.12
7 hr	n.d.	0.07

n.d. = Not determined

phenanthrene as -0.11 hr^{-1} and 6.3 hr, respectively, in distilled water at 20 °C using a high pressure mercury lamp. The shorter half life obtained for phenanthrene in the present study compared to the half life reported by Fukuda *et al.* (1988) may be due to the use of seawater, which increases the rate of photodegradation several times over that in distilled water (Fukuda *et al.*, 1988).

4.4.2 Extrapolation of Phenanthrene Photodegradation Half Life to Florida Summer Sunlight (30 °N)

The use of the particular lamp source (xenon arc, 1.8 kW) herein is its first use for photolysis studies of petroleum. The lamp was found to be the best alternative commercial artificial source to sunlight in terms of its spectral characteristics as discussed in Section 4.1.1. It has also been reported (e.g. Parker and Leahey, 1988; de Bertrand and Barceló, 1991) that this lamp provides a good model for the fate of pesticides under simulated natural environmental photodegradation conditions.

In order to relate the rate of degradation caused by the xenon lamp to the rate likely to occur in sunlight, the light intensity from the xenon lamp incident on the sample was compared with global radiation (e.g. Florida summer sunlight, latitude 30 °N, 12 hour of light per day).

Parker and Leahey (1988) derived a conversion equation which shows this relationship as:

Assuming 12 hr of daylight,

$$\text{1 day Florida sunlight} \equiv \frac{0.75 \times 12 \times (0.2014 \times 10^3)}{0.335 \times Z} \text{ hr} \quad (1)$$

where Z (Wm^{-2}) is the intensity of xenon lamp incident on the sample surface. The variation in the radiation intensity of sunlight through the day was considered in the above equation. The light intensity of the lamp as measured was 194 Wm^{-2} (see Section 4.3.3). Thus substituting the value of Z in equation (1) gives the following relation:

$$\text{1 day Florida sunlight} \equiv 2.79 \text{ hr under the xenon lamp} \quad (2)$$

(assuming 12 hr of daylight)

Therefore as $t_{1/2}$ of phenanthrene was experimentally found to be (2.0-2.2 hr) under the xenon lamp, the corresponding $t_{1/2}$ under Florida midday, midsummer sunlight would be 8.6-9.5 hr according to equation (2) (at latitude 30°N). Similarly, the rate of degradation caused by the xenon lamp can be compared with other locations at different latitudes and seasons (see Mill, 1982; Parker and Leahey, 1988 for details).

4.4.3 Identification of Phenanthrene Photoproducts

The photoproducts identified in this experiment in order of GC elution were fluorene, fluorenone, 2,3:4,5-dibenzoxepin, 2,2'-diformylbiphenyl, 3,4-benzocoumarin and 9,10-phenanthrenequinone (Table 4.9; for mass spectra see Appendix 4) whereas in experiment 3 only fluorenone, 3,4-benzocoumarin and 2,3:4,5-dibenzoxepin were identified. The reason for detecting more products in the former experiment was the longer irradiation time which increased the yield, and the larger volume of sample injected into the GC-MS

Table 4.9 Relative GC retention times of phenanthrene photoproducts and comparison with authentic and literature values.

Compound	Formula	Molecular Weight	Relative Retention Time ^a		
			Photoproducts	Authentic compounds	Literature ^c
Fluorene	C ₁₃ H ₁₀	166	0.83	0.83	0.73
Fluorenone	C ₁₃ H ₈ O	180	0.96	0.96	0.96
2,3:4,5-Dibenzoxepin	C ₁₄ H ₁₀ O	194	0.99	- b -	0.99
Phenanthrene	C ₁₄ H ₁₀	178	1.00	1.00	1.00
2,2'-Diformylbiphenyl	C ₁₄ H ₁₀ O ₂	210	1.06	- b -	1.15
3,4-Benzocoumarin	C ₁₃ H ₈ O ₂	196	1.12	1.12	1.24
9,10-Phenanthrenequinone	C ₁₄ H ₈ O ₂	208	1.28	1.28	1.53

^a Retention times expressed in minutes relative to retention time of phenanthrene.^b Standard was not available.^c Patel *et al.* (1978).

which increased the limit of detection and allowed more accurate quantification.

Comparison of the relative retention time (RRT) of the authentic photoproducts to phenanthrene with the photoproducts formed after irradiation confirmed the identification (Table 4.9). When compared with a previous study (Patel *et al.*, 1978) a good agreement for compounds eluted before phenanthrene was observed, but compounds eluting after phenanthrene had 0.1-0.2 RRT shorter than those analysed by Patel *et al.* (1978). This difference could be due to differences in GC column specifications.

Almost all of the products were found in the pentane extract of the samples (Figure 4.16) while the remainder of some was detected in the DCM extract. In general terms the concentration of these products was very small (the highest was 40 ng mL⁻¹, Table 4.10) but increased with time of exposure (Figure 4.17). 3,4-benzocoumarin had the highest yield followed by fluorenone and 2,2'-diformylbiphenyl (Table 4.10). 2,3:4,5-dibenzoxepin and 9,10-phenanthrenequinone were present in much smaller yields. These degradation products which formed as a result of exposing phenanthrene to the xenon lamp are also likely to form under the action of sunlight.

It is interesting to note how a single hydrocarbon can generate several different products when photooxidised. Therefore when considering a complex substrate such as a crude oil slick in the marine environment with constituents exhibiting efficient light absorption over a broad spectrum an unlimited transformation into complex compounds, mostly with enhanced water solubility, may occur. Such a situation was experienced in studies carried out in the Arabian Gulf after oil spills (e.g. Literathy, 1992; Ehrhardt and Burns, 1993).

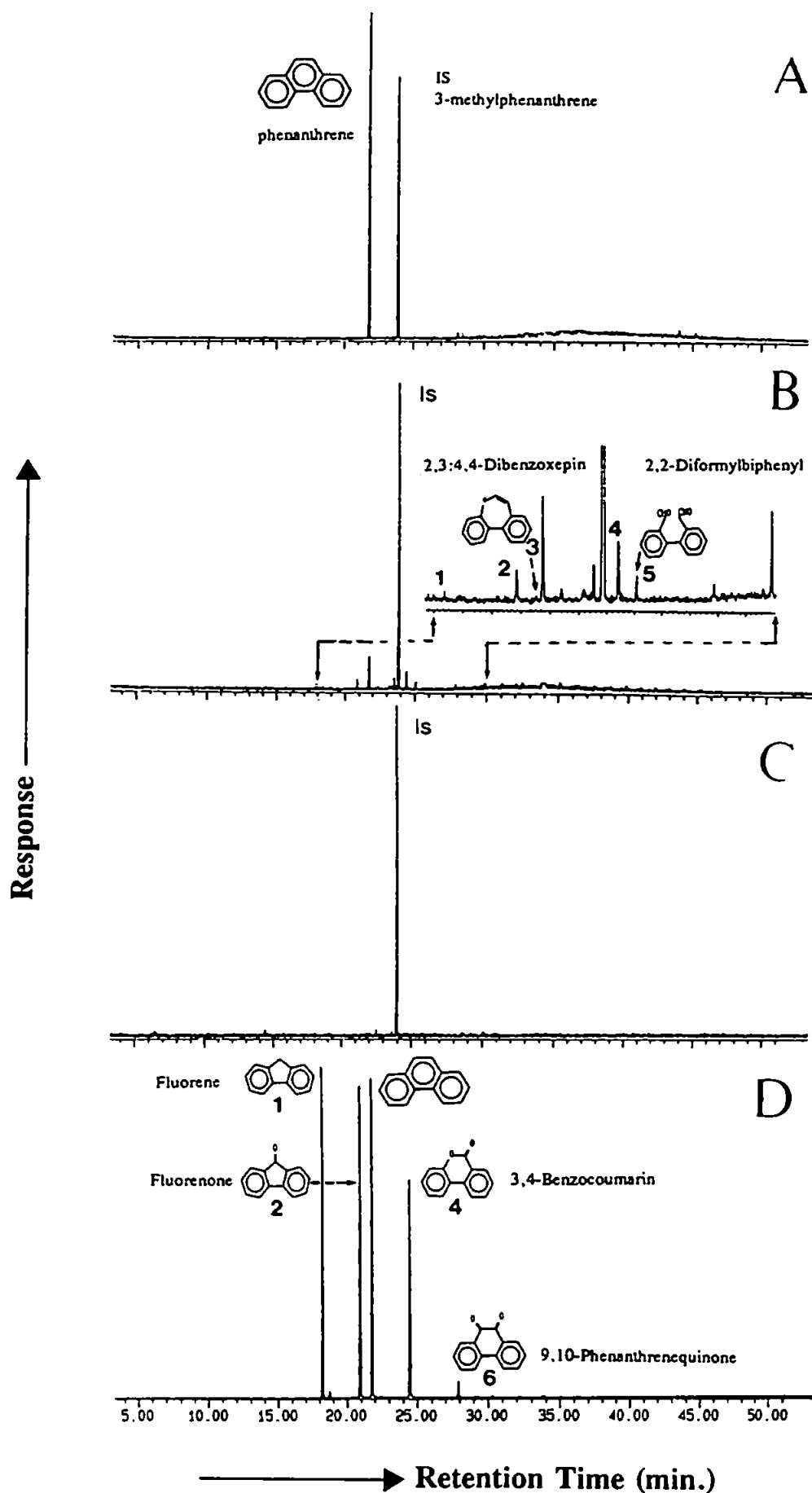


Figure 4.16 TIC chromatograms of pentane extract of (A) phenanthrene at 0 hr irradiation; (B) phenanthrene after 7 hr of irradiation under xenon lamp; (C) irradiated seawater and (D) standard mixture of the authentic photoproducts.

Table 4.10 Concentration of phenanthrene photodegradation products as formed with irradiation time.

Compound	Formula	Concentration ng mL ⁻¹ ^a									
		1 hr		2 hr		4 hr		6 hr		7 hr	
Fluorene	C ₁₃ H ₁₀	2	4.8 %	2	6.5 %	1.7	3.6 %	5	4.5 %	2.7	3.2 %
Fluorenone	C ₁₃ H ₈ O	20 ^b	47.6 ^b %	4	12.9 %	7	15 %	20	18.3 %	20	23.3 %
2,3:4,5-Dibenzoxepin	C ₁₄ H ₁₀ O	7	16.7 %	8	25.8 %	7	15 %	10	9.2 %	5	5.8 %
2,2'-Diformylbiphenyl	C ₁₄ H ₁₀ O ₂	7	16.7 %	7	22.6 %	7	15 %	20	18.3 %	18	21 %
3,4-Benzocoumarin	C ₁₃ H ₈ O ₂	6	14.3 %	10	32.3 %	20	42.2 %	40	36.7 %	30	35 %
9,10-Phenanthrenequinone	C ₁₄ H ₈ O ₂	n.d	n.d	n.d	n.d	4	8.6 %	14	12.8 %	10	11.7 %
Total Concentration of identified products		42 ^b		31		46.7		109		85.7	

^a Percentage values in the table are calculated on the basis of the concentration of the total identified photo-products

^b Cross contamination by fluorenone

n.d = not detected

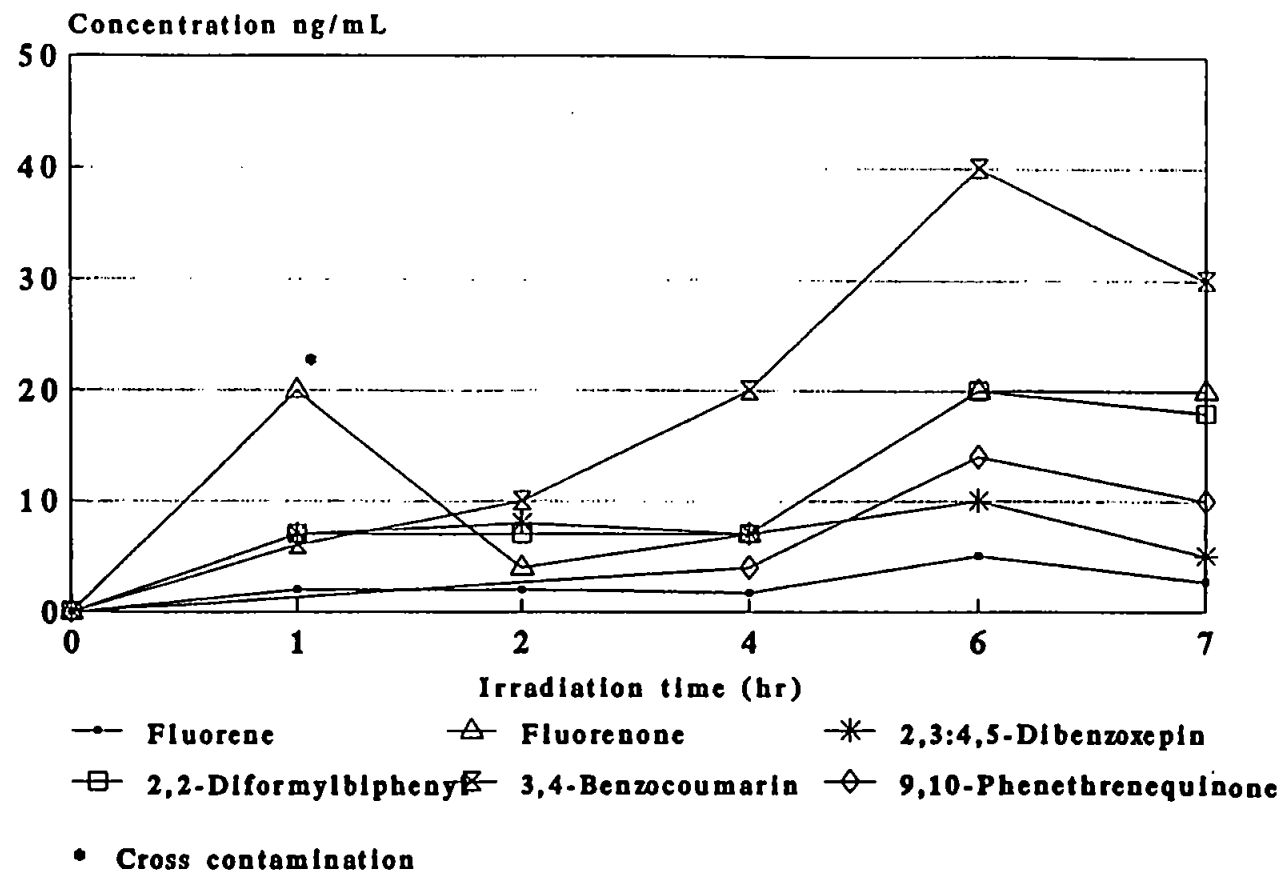


Figure 4.17 The distribution of the products formed during photodegradation of phenanthrene as a function of time determined by GC-MS.

No additional products could be identified in the DCM extracts even after methylation with iodomethane. As seen from Table 4.10 the concentration of the products identified was very small, therefore if there were any acidic products formed upon irradiation, they would have probably been present in low concentrations and would not be efficiently recovered especially after the lengthy derivatisation procedure. Using larger volumes of phenanthrene solutions for photolysis may enhance the identification and quantification of the undetected photoproducts in this experiment.

However, the total amount of photoproducts was 11.64% of the initial mass of phenanthrene after 7 hr of irradiation (Table 4.11). Figure 4.18 presents a flow chart of the fate of phenanthrene photodegraded for seven hours under the xenon lamp. Hence, the results indicate that there are other intermediates undetected. It could be possible that some non-volatile high molecular weight products were formed by polymerisation (Thominette and Verdu, 1984a,b), or it could be that the products formed are thermally unstable and therefore degrade in the GC injection port as demonstrated by some of the photoproducts of toluene (Syndes *et al.*, 1985a). Photopolymerisation is unlikely because it requires simultaneous photooxidation and collision to occur in solution. Collision probability in a dilute solution is low. The possibility that some of these products are too volatile to be analysed may be another explanation. Oxidation of phenanthrene to carbon dioxide is possible as found for other substrates (Parker and Leahey, 1988). One method to test this assumption is to carry out a photodegradation study using ^{14}C radiolabelled phenanthrene and to quantify the $^{14}\text{CO}_2$ production and any other products (see Readman, 1982).

Patel *et al.* (1978) have also identified the above mentioned products and other oxygenated acidic products upon irradiation with a visible light source (500 W tungsten lamp) in the

Table 4.11 Quantitative budgeting of the fate of phenanthrene after seven hours of irradiation under xenon lamp determined by GC-MS.

Mass of phenanthrene at 0 hr irradiation	23.19 μg
Mass of phenanthrene remained after 7 hr irradiation.	1.99 μg (8.58 %)
Mass of phenanthrene photodegraded after 7 hr irradiation.	21.2 μg (91.41 %)
Total mass of identified photo-products after 7 hr irradiation.	2.7 μg (11.64 %)*
Total mass of unidentified photo-products after 7 hr irradiation.	18.5 μg (79.77 %)*

* Percentage of the identified photo-products from the total mass of phenanthrene at 0 hr irradiation.

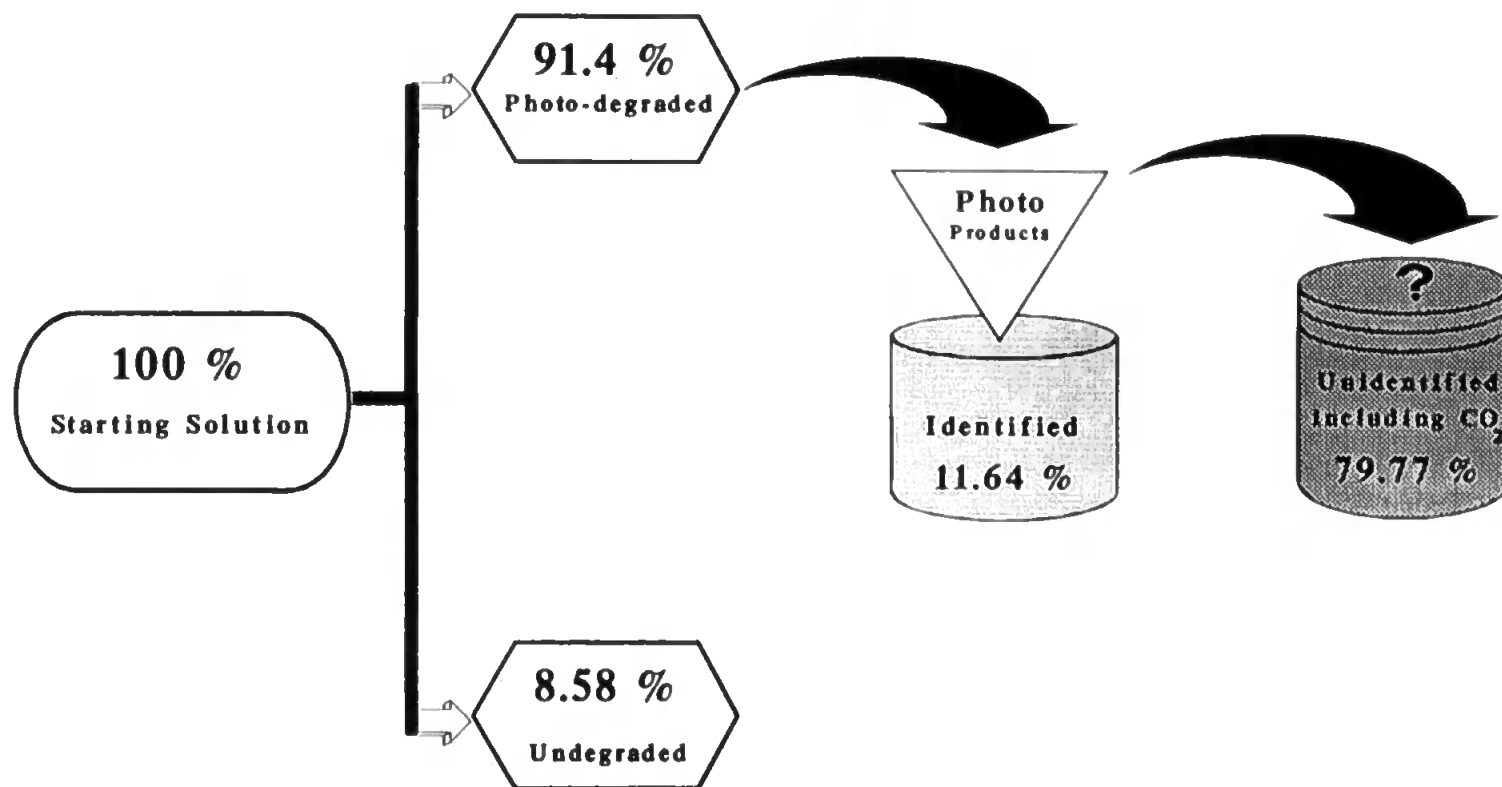


Figure 4.18 Budget flow chart of the fate of phenanthrene photodegraded under xenon lamp after 7 hr irradiation.

presence of oxygen and methylene blue, a known singlet oxygen sensitiser, although the yields were not reported. However, it is interesting to note that the identified products in the present study were formed without an artificial sensitiser or external source of oxygen. This suggests that phenanthrene can undergo a direct photooxidation with the available oxygen in seawater since phenanthrene absorbs UV light above 300 nm, and has a high quantum efficiency (0.87-0.94) (Wintgens, 1989).

The photooxidation of PAH via a singlet oxygen mechanism was previously shown for phenanthrene and anthracene (e.g. Dowty *et al.*, 1974; Ranby and Rabek, 1975). Zepp (1988) pointed out that singlet oxygen is a highly selective oxidant reacting rapidly only with electron-rich compounds such as polycyclic aromatic hydrocarbons. Also, singlet oxygen is more powerful than dioxygen (Zepp *et al.*, 1985) and can be formed even if oxygen is present in only trace amounts (Dupont *et al.*, 1990).

The reaction of phenanthrene with singlet oxygen can be explained as follows. In the first stage, phenanthrene absorbs UV light and is excited to a longer-lived triplet state. Subsequently reaction occurs between the triplet state of phenanthrene and molecular oxygen (dioxygen) with the formation of singlet oxygen. The energy required to excite dioxygen to its first singlet state is only 94 kJ mole⁻¹ (Zepp *et al.*, 1985). Since the energy of the triplet state of phenanthrene above the ground state is 258 kJ mole⁻¹ (Carmichael and Hug, 1989), it is well above the energy required to excite dioxygen to singlet oxygen. The singlet oxygen reacts with another molecule of phenanthrene to give a peroxide which is subjected to further photochemical transformation with the ultimate formation of ketones, acids and other oxygenated products as shown in **Table 4.9**.

The primary product in a phenanthrene singlet oxidation process was suggested to be 9,10-epoxy-9,10-dihydrophenanthrene (Figure 4.19) which upon irradiation undergoes interconversion to 2,3:4,5-dibenzoxepin, fluorene, fluorenone, 2,2'-diformylbiphenyl, 9,10-phenanthrenequinone and other products (Dowty *et al.*, 1974). Although all of these products were detected in this study, the primary product, 9,10-epoxy-9,10-dihydrophenanthrene, was not. Absence of 9,10-epoxy-9,10-dihydrophenanthrene in the present study implies that if it is a primary intermediate in the photodegradation of phenanthrene as suggested by Dowty *et al.* (1974), it must have been very short lived compared to other identified photoproducts. In addition, concurrent appearance of photoproducts; fluorene, fluorenone, 2,2'-diformylbiphenyl, 2,3:4,5-dibenzoxepin, 9,10-phenanthrenequinone suggests these are produced competitively from 9,10-epoxy-9,10-dihydrophenanthrene, and they in turn are intermediates in the production of more polar (oxygenated) photoproducts including ultimately CO₂.

The reaction of phenanthrene with ground state oxygen was reported to give entirely different products (Dowty *et al.*, 1974). This supports the formation of these products via a singlet oxygen mechanism.

The identified photoproducts can also be formed by other photochemical reactions, for example, 2,2'-diformylbiphenyl was identified as the major product from the reaction of phenanthrene with ozone (Yoshikawa *et al.*, 1987).

Ultraviolet Fluorescent Analysis of Irradiated Phenanthrene Samples from Experiment 4

The aliquots (10 mL) withdrawn from the irradiated and non-irradiated phenanthrene solutions were also examined by UVF as an additional characterisation method to GC-MS.

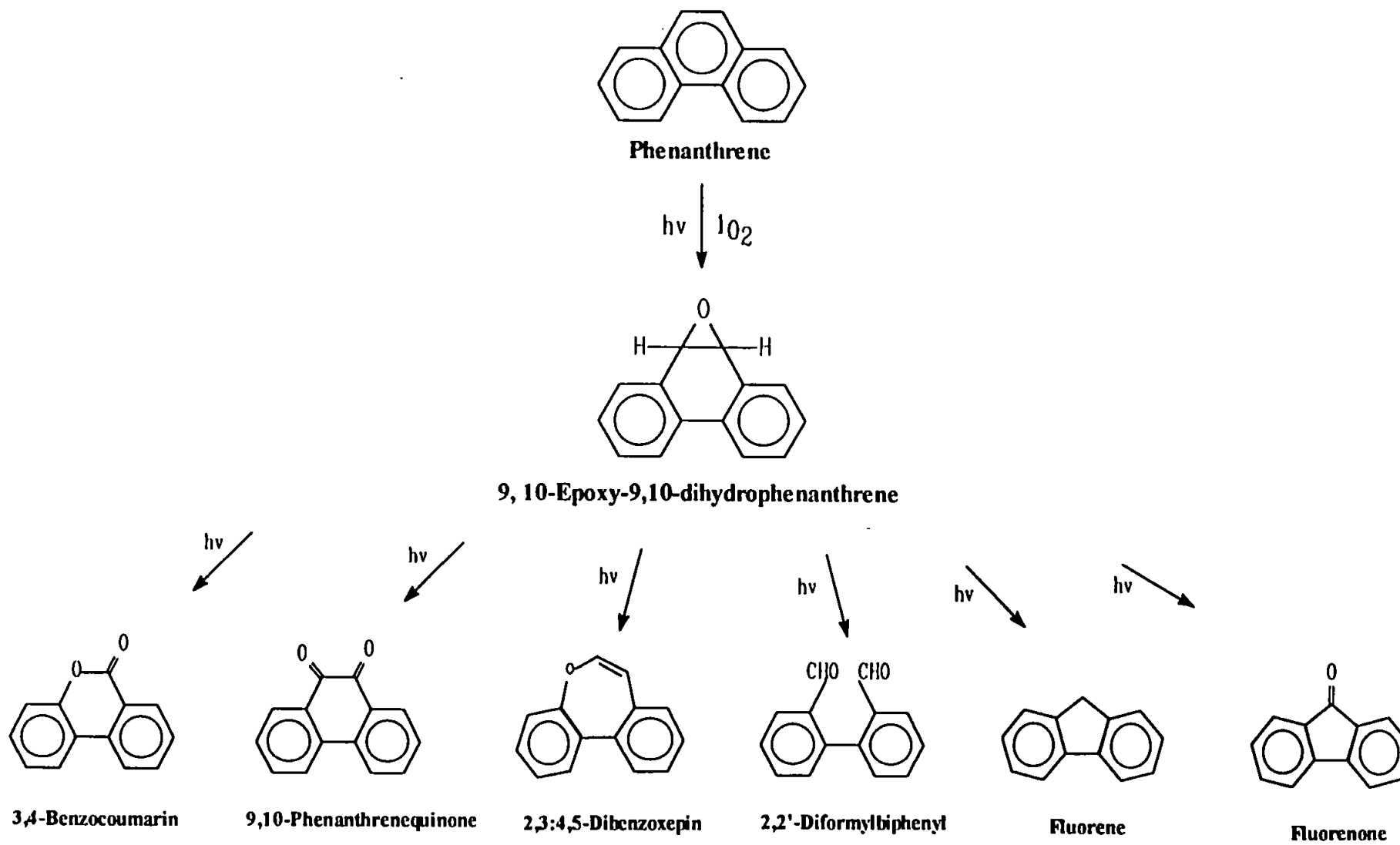


Figure 4.19 Photooxidation pathway of phenanthrene and formation of photoproducts.

The UVF calibration curve constructed from phenanthrene in seawater showed a linear response to $0.8 \mu\text{g mL}^{-1}$ (Figure 4.20). From the graph, the concentration of phenanthrene samples (0-7 hr irradiation) was obtained (Table 4.12) which showed a decrease in initial concentration from 100% to 22% after 7 hours of irradiation, resulting in 78% degradation. The seawater blanks (irradiated and non-irradiated) showed a negligible fluorescence intensity at the measured wavelength ($< 0.001 \mu\text{g mL}^{-1}$).

When these concentrations were compared with concentrations obtained by GC-MS, reasonable agreement was demonstrated (Table 4.13) and allowed for a direct comparison between the two methods of analysis. The agreement between these two methods is interesting because UVF is usually considered at best a semi-quantitative method (Shiu *et al.*, 1990). This is certainly true for a solutions containing numerous fluorescing and non-fluorescing compounds such as an oil extract (e.g. SWSF of crude oil) as seen from Chapter 2 but the present results with a single compound (i.e. phenanthrene) show that UVF is a quantitative method provided that the analysis conditions are carefully selected (especially the calibrant and the wavelength). Examination of the synchronous scanning spectra of irradiated phenanthrene samples did not show emissions from photoproducts at longer wavelengths beyond phenanthrene emission wavelengths. However, the analysis of the authentic standards established that these photoproducts mostly emit at shorter wavelengths (Table 4.14), so perhaps the emissions in the irradiated samples have been masked by pentane, used to rinse the cells. Moreover, when fluorenone was measured at an equimolar concentration to phenanthrene, a 4.8% emission compared to that of phenanthrene (both measured at their maximum excitation wavelength and under the same UVF analysis conditions) was observed. Similarly, the emission of 9,10-phenanthrenequinone and 3,4-benzocoumarin were calculated compared to phenanthrene,

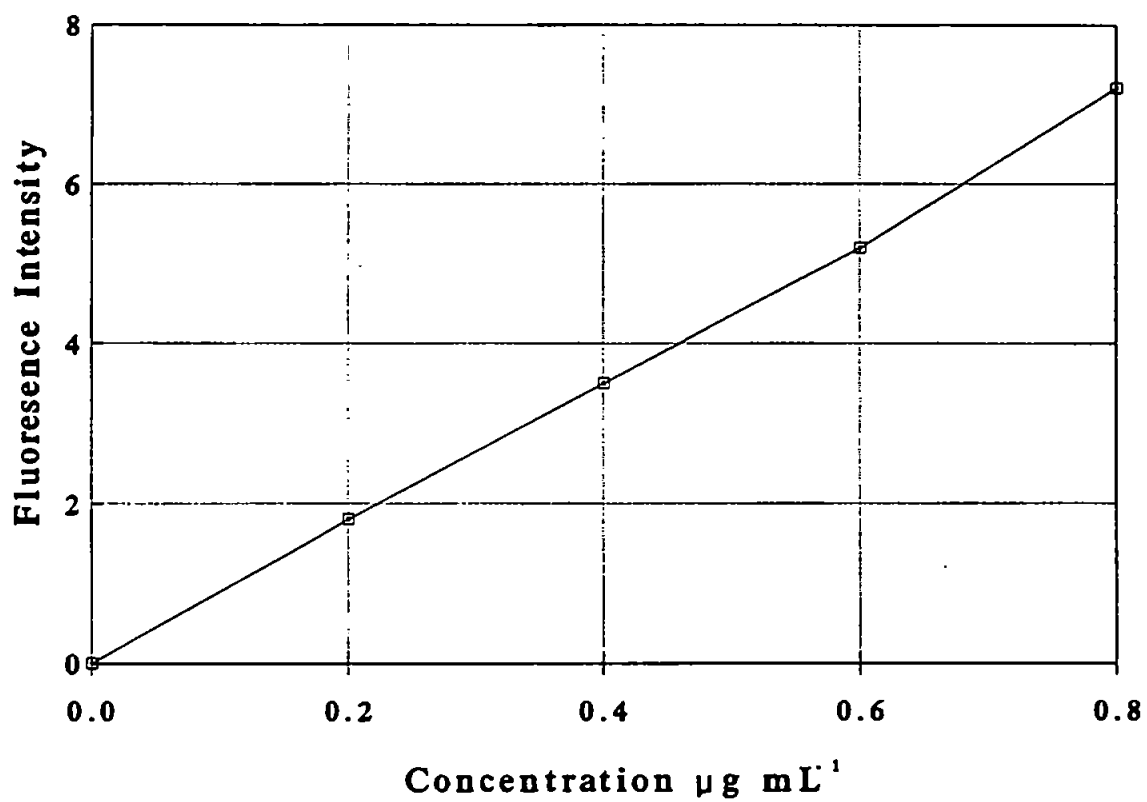


Figure 4.20 UVF calibration curve of phenanthrene in seawater.

Table 4.12 UVF measurement of phenanthrene samples irradiated for 0-7 hr under xenon lamp in experiment (4).

Sample	Concentration $\mu\text{g mL}^{-1}$ ^a
0 hr	0.69
1 hr	0.62
2 hr	0.52
4 hr	0.41
6 hr	0.22
7 hr	0.15

^a Concentration expressed as phenanthrene equivalent.

Table 4.13 Direct comparison between GC-MS and UVF results for the photodegradation of phenanthrene under the xenon lamp as obtained from experiment (4).

Sample	Concentration $\mu\text{g mL}^{-1}$	
	GC-MS ^a	UVF ^b
0 hr	0.77	0.69
1 hr	0.47	0.62
2 hr	0.42	0.52
4 hr	0.28	0.41
6 hr	0.12	0.22
7 hr	0.07	0.15

^a Concentration was determined with reference to 3-methylphenanthrene internal standard.

^b Concentration expressed as phenanthrene equivalent.

Table 4.14 UVF analysis of phenanthrene authentic photoproducts.

Compound	Excitation Wavelength max. (nm)	Emission Wavelength (nm)
Phenanthrene	250	348,364,384
Fluorene	263	303,310
Fluorenone	256	262,303
9,10-phenanthrenequinone	265	285,303,385,400
3,4-benzocoumarin	270	292,375

For analysis conditions see text.

all at their maximum excitation wavelengths, and found to be 3.6% and 2.4%, respectively. This means that the emission of these photo-products will be small when present in low concentrations in a mixture with phenanthrene. The exception is fluorene which has 12.6 times higher fluorescence emission than phenanthrene as also observed by Ehrhardt *et al.* (1992). However, the very low concentration of fluorene as measured by GC-MS (highest concentration was 5 ng mL⁻¹ after 6 hours, see Table 4.10) would not allow detectable emission, even considering the above.

While the toxicity of phenanthrene may be restricted by its solubility (Futoma *et al.*, 1981), the incorporation of oxygen in some of the products would enhance their solubility and make them available to marine organisms. Although the absolute concentration of these photo-products in water could be low as seen from this study, they could be extensively concentrated by organisms leading to biological effects. Data on the toxicity of some of these photoproducts is limited, but for instance, 2,2'-diformylbiphenyl exerted toxic effects on rats (Yoshikawa *et al.*, 1987).

4.5 Conclusions

Phenanthrene served as a useful model for petroleum aromatic compounds for the study of the photodegradation of SWSF of Kuwait crude oil because of its ability to absorb light in the high UV and visible range with subsequent direct photodegradation and its sufficient solubility in water. Simulation of solar irradiation methodology has been successfully established using a calibrated 1.8 kW filtered xenon lamp, after three progressive preliminary experiments which revealed the following:

Experiment 1; showed a rapid decrease in the initial phenanthrene present from 100% to 4% in 3 hours. This was due to temperature increasing during exposure.

Experiment 2; better control of the temperature resulted in a decrease in the rate of the degradation and less scatter in the data. Thus phenanthrene fell from 100% to 48.5% at 3 hours of irradiation relative to initial concentration .

Experiment 3; good control of the temperature at 25 ± 3 °C with a high power chiller gave more controlled degradation, with the concentration of phenanthrene decreasing from 100% to 51% relative to initial concentration in 2 hours of irradiation. A slower degradation proceeded thereafter reaching 74% after 4 hours. The photodegradation was found to follow a pseudo first-order reaction. The photodegradation rate constant (k_p) was $-0.342 \pm 0.0025 \text{ hr}^{-1}$ and half life ($t_{1/2}$) was calculated as 2.03 hr. Some photodegradation products were detected and quantified but amounted to only a very small percentage of the total photodegraded phenanthrene. No additional products were identified after derivatization ($\text{BF}_3/\text{methanol}$).

The reproducibility of the optimised irradiation method was proven in a fourth experiment, in which the photodegradation rate constant (k_p) was -0.317 ± 0.029 and $t_{1/2}$ was 2.2 hr at 25°C. Extrapolating the $t_{1/2}$ determined from experiment 3 and 4 to latitude 30°N (Florida midday, midsummer) showed that these compound would be photodegraded in 8.6-9.5 hr.

Quantitative determination of the photodegradation of phenanthrene by direct UVF analysis demonstrated a reasonable agreement with that obtained by GC-MS and allowed for direct comparison between the two methods of analysis.

The direct photooxidation of phenanthrene resulted in the formation of a number of identified photoproducts as detected by GC-MS. These were almost totally found in the pentane extracts, and included: fluorene, fluorenone, 2,3:4,5-dibenzoxepin, 2,2'-diformylbiphenyl, 3,4-benzocoumarin and 9,10-phenanthrenequinone. However, the concentrations were low (11.6 % of the initial mass of phenanthrene).

The good agreement between UVF and GC-MS tracking of photo-disappearance of phenanthrene was explained by the low fluorescence yield of all the photodegradation products.

The established irradiation methodology has proved to be reliable and valid and can be used for the irradiation of the seawater soluble fraction of Kuwait crude oil in order to determine the photodegradation rates and half lives of the constituents under relevant environmental conditions.

CHAPTER FIVE

CHAPTER FIVE

PHOTODEGRADATION OF THE SEAWATER SOLUBLE FRACTION OF KUWAIT CRUDE OIL

5.1 Introduction

Despite increasing oil contamination of the marine environment, a complete understanding of the mechanisms involved in the weathering of oil is still lacking. It is generally accepted that the fate of crude oil which is released into the marine environment is determined by a number of physical processes, including spreading, evaporation, dissolution and emulsification. Such processes lead to the dispersal of the bulk of the oil and also contribute to biodegradation and photodegradation which alter the chemical composition of the spilled oil (reviewed by NAS, 1985). It has been shown, for instance, that photooxidation is responsible for a detectable increase in the nonvolatile residual fraction of weathered oil (Burwood and Speers, 1974) and also for changes in oil viscosity (Sokolov *et al.*, 1986).

Photodegradation can occur on both the surface exposed portion of an oil slick and within that part of the oil which leaches into the underlying water- the seawater soluble fraction- which can be reached by sunlight. In both phases, photochemical transformation can occur, though it has been found that the presence of an efficient singlet oxygen sensitiser in the crude oil increases reactivity (Thominette and Verdu, 1984a,b; Sydnes *et al.*, 1985b). This and other aspects of oil photooxidation have been discussed in some detail in the introduction to the preceding chapter.

Attempts have been made to study the photochemical reactions of oil in laboratory simulation systems (e.g. Tjessem and Aaberg, 1983; Literathy *et al.*, 1991) and in the open sea (e.g. Ehrhardt, 1987; Ehrhardt and Burns, 1993). Such studies were of a limited nature and the results were sometimes difficult to interpret. This is mainly because irradiation of a whole crude oil causes a complex and dynamic process which involves several concurrent photooxidation mechanisms and the formation of complex products. In addition, non specific monitoring methods were used. Other studies have also excluded important environmental factors such as the use of natural seawater, simulated natural radiation and constant irradiation temperature.

5.2 Aims

In the present study an attempt was made to examine the effects of solar-simulated photolysis on the degradation of a relatively simple oil-in-water mixture. This was achieved by following the photodegradation kinetics of individual components of a seawater soluble fraction (SWSF) of Kuwait crude oil.

The irradiation system previously constructed and tested on phenanthrene (see Chapter 4) provided a reproducible and validated method to obtain information on the abiotic chemical pathway of SWSF decomposition in seawater.

5.3 Experimental

All material, glassware, instruments and experimental methods have been described in Chapter 4, Section 4.3. The preparation of a homogeneous solution of sea water soluble fraction (SWSF) of Kuwait crude oil has been described in Chapter 2, Section 2.4.2.

SWSF samples (50 mL) were irradiated for 1,2,4,6,8,14,18,24 and 48 hr at 25 ± 2 °C under the xenon lamp. These irradiation times were chosen to include both shorter (< 12 hr) and longer (> 24 hr) periods which would cover a broad range of the degradation process. Included in the experiment were seawater blanks, (irradiated for 48 hr and non-irradiated), and a dark control containing SWSF.

After irradiation, deuterated benzene (50 μ g), naphthalene (10 μ g) and phenanthrene (5 μ g) were added to the samples which were then extracted (see Chapter 3.3.2) and prepared for analysis with an autosampler by cryogenically cooled GC-MS under conditions described in Chapter 3, Section 3.3.14. Care was taken during the irradiation, preparation and analysis of samples to ensure that all samples were uniformly treated to reduce sources of variation.

Total ion chromatograms (TIC) were obtained for each irradiated SWSF sample and the total peak area of each identified compound was calculated by integration. Isomers which co-eluted were integrated as one peak as described in Chapter 3, Section 3.3.7. Concentrations were calculated with reference to the deuterated internal standards integrated with respect to their molecular ions. The seawater blanks showed clear chromatograms, therefore no interference with the samples are expected.

5.4 Results and Discussion

5.4.1 Assessment of the Recovery of Seawater Hydrocarbons

The concentrations of SWSF components of Kuwait crude oil obtained after irradiation from 0 to 48 hours under the xenon lamp are given in Table 5.1. The components of

Table 5.1 Concentration of the seawater soluble fraction compounds of Kuwait crude oil with respect to time of irradiation under xenon lamp at 25°C.

Compound	Concentration ($\mu\text{g mL}^{-1}$) after irradiation									
	0 hr	1 hr	2 hr	4 hr	6 hr	8 hr	14 hr	18 hr	24 hr	48 hr
Benzene	1.30	1.28	1.46	1.47	1.47	1.20	1.36	1.13	1.58	1.41
Toluene	13.35	13.51	16.37	15.91	15.64	12.14	14.03	11.48	17.12	15.04
Ethylbenzene	2.84	2.84	3.26	3.38	3.75	2.28	2.80	2.18	3.54	3.14
1,3-Dimethylbenzene + 1,4-Dimethylbenzene	7.52	7.40	8.44	8.76	9.46	6.10	7.33	5.68	9.09	7.96
1,2-Dimethylbenzene	5.41	5.11	5.76	5.92	6.32	4.28	5.07	4.10	5.98	5.35
Isopropylbenzene	0.21	0.21	0.24	0.24	0.26	0.16	0.20	0.15	0.26	0.23
<i>n</i> -Propylbenzene	0.27	0.26	0.31	0.31	0.35	0.19	0.25	0.19	0.33	0.27
1-Ethyl-3-methylbenzene + 1-Ethyl-4-methylbenzene	1.61	1.59	1.86	1.90	2.07	1.27	1.56	1.20	1.99	1.67
1,3,5-Trimethylbenzene	0.49	0.48	0.54	0.54	0.56	0.37	0.45	0.33	0.55	0.44
1-Ethyl-2-methylbenzene	1.32	1.30	1.45	1.44	1.49	0.99	1.23	0.95	1.48	1.28
1,2,4-Trimethylbenzene	2.38	2.22	2.48	2.47	2.52	1.67	1.83	1.35	1.97	0.91
1,2,3-Trimethylbenzene	1.21	1.08	1.24	1.24	1.22	0.88	1.06	0.85	1.18	0.94
<i>sec</i> -Butylbenzene	0.05	0.05	0.06	0.05	0.05	0.03	0.03	0.02	0.00	0.00

"continued..."

Table 5.1 "continued"

Compound	Concentration ($\mu\text{g mL}^{-1}$) after irradiation									
	0 hr	1 hr	2 hr	4 hr	6 hr	8 hr	14 hr	18 hr	24 hr	48 hr
1-Isopropyl-3-methylbenzene + 1-Isopropyl-4-methylbenzene	0.34	0.32	0.36	0.36	0.38	0.25	0.31	0.24	0.35	0.26
1-Isopropyl-2-methylbenzene	0.08	0.09	0.10	0.07	0.10	0.07	0.11	0.09	0.11	0.08
1,3-Diethylbenzene	0.20	0.22	0.23	0.24	0.28	0.17	0.24	0.18	0.30	0.33
1-Methyl-3-propylbenzene + 1,4-Diethylbenzene + 1,3-Dimethyl-5-ethylbenzene + 1,2-Diethylbenzene	0.32	0.31	0.33	0.36	0.38	0.24	0.28	0.23	0.36	0.38
1-Methyl-2-propylbenzene	0.18	0.18	0.19	0.21	0.24	0.16	0.22	0.19	0.30	0.30
1,4-Dimethyl-2-ethylbenzene + 1,3-Dimethyl-4-ethylbenzene	0.63	0.59	0.61	0.64	0.66	0.41	0.44	0.33	0.48	0.23
1,2-Dimethyl-4-ethylbenzene	0.18	0.17	0.16	0.18	0.19	0.12	0.12	0.09	0.11	0.03
1,3-Dimethyl-2-ethylbenzene	0.05	0.03	0.04	0.03	0.03	0.03	0.04	0.02	0.04	0.03
1,2-Dimethyl-3-ethylbenzene	0.19	0.15	0.19	0.18	0.19	0.13	0.18	0.13	0.19	0.14

"continued..."

Table 5.1 "continued"

Compound	Concentration ($\mu\text{g mL}^{-1}$) after irradiation									
	0 hr	1 hr	2 hr	4 hr	6 hr	8 hr	14 hr	18 hr	24 hr	48 hr
1,2,4,5-Tetramethylbenzene + 1,2,3,5-Tetramethylbenzene	0.265	0.245	0.255	0.236	0.227	0.153	0.098	0.061	0.069	0.018
1,2,3,4-Tetramethylbenzene	0.707	0.625	0.739	0.689	0.666	0.453	0.498	0.365	0.428	0.26
Naphthalene	0.089	0.085	0.088	0.082	0.074	0.062	0.062	0.045	0.042	0.010
2-Methylnaphthalene	0.128	0.125	0.131	0.108	0.096	0.084	0.064	0.042	0.035	0.000
1-Methylnaphthalene	0.151	0.135	0.130	0.114	0.100	0.080	0.076	0.064	0.045	0.000
1+2-Ethylnaphthalene	0.024	0.018	0.019	0.015	0.015	0.013	0.010	0.006	0.005	0.003
2,6-Dimethylnaphthalene + 2,7-Dimethylnaphthalene	0.028	0.023	0.015	0.030	0.024	0.015	0.022	0.014	0.016	0.000
1,3-Dimethylnaphthalene + 1,7-Dimethylnaphthalene	0.059	0.042	0.048	0.046	0.039	0.025	0.028	0.022	0.025	0.000
1,6-Dimethylnaphthalene	0.043	0.043	0.049	0.034	0.034	0.029	0.029	0.016	0.014	0.000
2,3-Dimethylnaphthalene + 1,4-Dimethylnaphthalene + 1,5-Dimethylnaphthalene	0.042	0.031	0.035	0.031	0.028	0.022	0.023	0.018	0.016	0.000

"continued..."

[illegible]

SWSF were measured by comparison with internal standards which automatically corrects for recovery. The recovery of deuterated internal standards through the work-up procedure was determined by analysing a mixture of the standards separately after work-up and comparing recoveries with an external standard mixture of the same compounds. The recovery of benzene-d₆ was found acceptable (mean 39.8%, SD 7.9; RSD 19.7%) considering the volatility of this chemical (Table 5.2). The mean recovery percentages of naphthalene-d₈ (mean 79.2%; SD 17.5; RSD 22%) and phenanthrene-d₁₀ (mean 70.9%; SD 18.5; RSD 26.2%) were also acceptable.

Encouragingly, the recovery of internal standards in SWSF samples was even better than for the internal standards alone (see Chapter 3, Table 3.5). The enhanced recoveries were due to the presence of co-solutes (i.e SWSF compounds) which increased the overall concentration strength of the solution during reconcentration by the Kuderna-Danish evaporative concentrator (K-D). The concentration of the solution to be concentrated is a crucial factor in the K-D recovery as discussed in Chapter 3, and hence the presence of the SWSF compounds improved the retention of the internal standards in the solution during the concentration process. Improvements in sample recovery due to co-solutes has been reported for other substrates (Chau and Lee, 1982; Ferreira *et al.*, 1993).

5.4.2 Photodegradation Kinetics of SWSF Compounds

Table 5.1 shows the behaviour of components which are photostable such as benzene and others which are photolabile such as naphthalene (Figure 5.1). The degradation of the photolabile SWSF compounds appeared to follow first-order kinetics with respect to time, as expressed by the equation:

$$C_t = C_0 e^{-k_p t} \quad \text{_____} \quad (1)$$

Table 5.2 Recovery (%) of deuterated internal standards added to irradiated SWSF for quantification for sample work up measured by comparison with a known concentration of external standards

Internal Standard	SWSF Sample Tube Number												
	0	1	2	4	6	8	14	18	24	48	Mean (n=10)	S.D.	R.S.D. (%)
Benzene-d ₆	40.1	51.6	36.9	40.0	48.9	32.5	30.1	37.1	31.4	49.8	39.8	7.9	19.7
Naphthalene-d ₈	79.8	98.9	74.5	85.4	105.4	60.2	56.9	67.7	64.0	99.5	79.2	17.5	22.1
Phenanthrene-d ₁₀	85.2	100.8	65.5	67.9	89.1	44.4	53.6	56.9	58.2	87.2	70.9	18.5	26.2

- The amounts of deuterated internal standard added were: 50 µg of benzene-d₆, 10 µg of naphthalene-d₈ and 5 µg of phenanthrene-d₁₀.
- All sample extracts were concentrated at 50 °C water bath temperature to 1 mL.

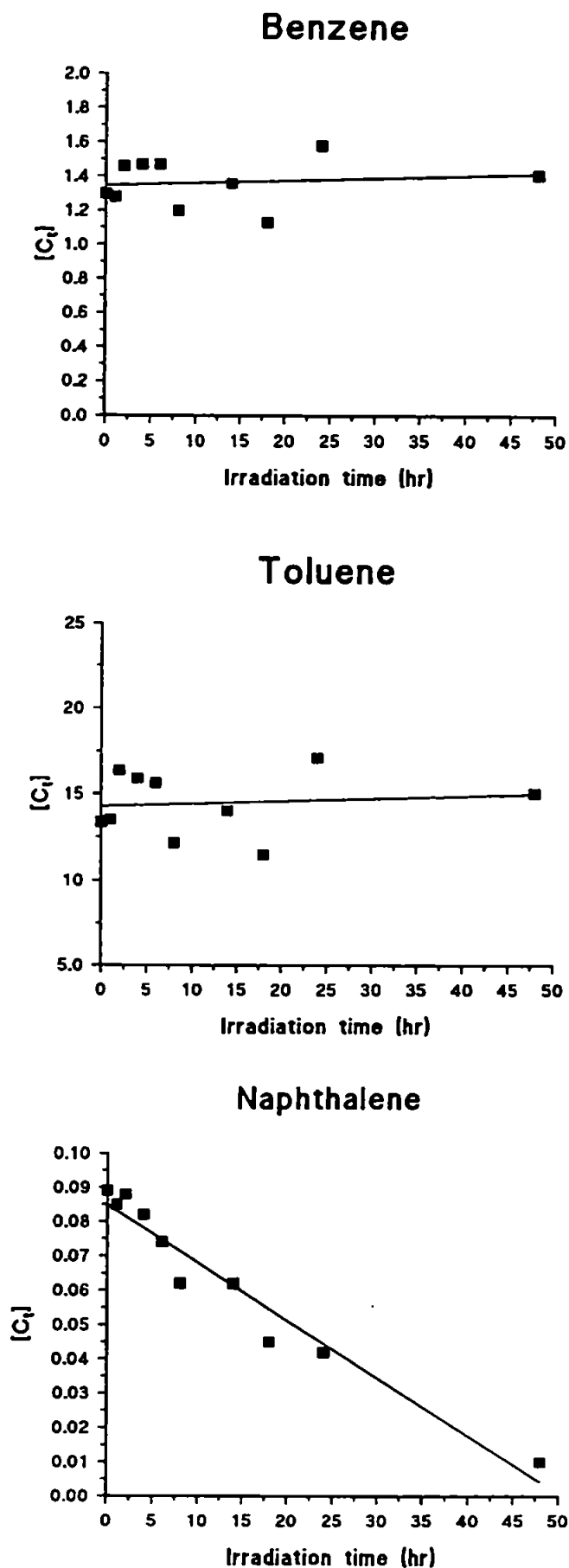


Figure 5.1 Concentration ($\mu\text{g mL}^{-1}$) of benzene, toluene and naphthalene determined with respect to time of irradiation under the xenon lamp.

Where C_0 and C_t are the concentration of hydrocarbon at the initial time (0) and at time t , and k_p is the first order photodegradation rate constant expressed in units of time^{-1} .

Transforming equation (1) by taking natural logarithm (Ln) results in:

$$\begin{aligned} \text{Ln}(C_t) &= \text{Ln}(C_0) - k_p t \\ \text{or} \quad \text{Ln}(C_t) - \text{Ln}(C_0) &= -k_p t \\ \text{or} \quad \text{Ln}(C_t/C_0) &= -k_p t \quad \text{_____} (2) \end{aligned}$$

Thus if a plot of $\text{Ln}(C_t/C_0)$ versus time is linear, then it can be concluded that the photodegradation reaction is pseudo first order, and the slope is equal to the first-order rate constant k_p . Another useful parameter is the photodegradation half life ($t_{1/2}$) which corresponds to the time taken for the concentration of photoreactive compound to decline to half life its original concentration (C_0).

i.e. $C_t = 0.5 C_0$

Substituting into equation (2) yields:

$$\begin{aligned} \text{Ln} \frac{0.5 C_0}{C_0} &= -k_p t_{1/2} \\ -0.693 &= -k_p t_{1/2} \\ t_{1/2} &= \frac{0.693}{k_p} \quad \text{_____} (3) \end{aligned}$$

The above kinetic treatment was applied to all components of SWSF tracked during the photodegradation experiment, and the results are presented in **Table 5.3**.

Photodegradation rates of the minor SWSF compounds, such as biphenyl,

Table 5.3 Photodegradation rate constant (k_p) and half lives of SWSF compounds of Kuwait crude oil under xenon lamp at 25 °C.

Compound	Statistical Analysis *					Rate Constant hr ⁻¹ ($k_p \pm S.E$)	Half Life ($t_{1/2}$) ^b
	r	r ²	p	t _{cal}	t _{crit}		
Benzene	0.139	0.019	0.701	0.40	2.31	n.d	n.d
Toluene	0.113	0.013	0.757	0.32	2.31	n.d	n.d
Ethylbenzene	0.036	0.001	0.920	0.10	2.31	n.d	n.d
1,3-Dimethylbenzene + 1,4-Dimethylbenzene	-0.012	0.000	0.974	0.03	2.31	n.d	n.d
1,2-Dimethylbenzene	-0.084	0.007	0.817	0.24	2.31	n.d	n.d
Isopropylbenzene	0.042	0.002	0.910	0.12	2.31	n.d	n.d
n-Propylbenzene	-0.073	0.005	0.841	0.21	2.31	n.d	n.d
1-Ethyl-3-methylbenzene + 1-Ethyl-4-methylbenzene	-0.052	0.003	0.886	0.15	2.31	n.d	n.d
1,3,5-Trimethylbenzene	-0.255	0.065	0.478	0.74	2.31	n.d	n.d
1-Ethyl-2-methylbenzene	-0.099	0.010	0.784	0.28	2.31	n.d	n.d
1,2,4-Trimethylbenzene	-0.045	0.202	0.193	1.42	2.31	n.d	n.d
1,2,3-Trimethylbenzene	-0.471	0.222	0.169	1.51	2.31	n.d	n.d

"continued..."

Table 5.3 "continued"

Compound	Statistical Analysis ^a					Rate Constant hr ⁻¹ (k _p ± S.E)	Half Life (t _{1/2}) ^b
	r	r ²	p	t _{cal}	t _{crit}		
<i>sec</i> -Butylbenzene	-0.930	0.865	0.000	6.20	2.45	-56.2 ± 9.1 x 10 ⁻³	12.3 hr
1-Isopropyl-3-methylbenzene + 1-Isopropyl-4-methylbenzene	-0.494	0.244	0.147	1.60	2.57	n.d	n.d
1-Isopropyl-2-methylbenzene	0.061	0.004	0.867	0.17	2.31	n.d	n.d
1,3-Diethylbenzene	0.583	0.339	0.077	2.00	2.31	n.d	n.d
1-Methyl-3-propylbenzene + 1,4-Diethylbenzene + 1,3-Dimethyl-5-ethylbenzene + 1,2-Diethylbenzene	0.192	0.037	0.594	0.55	2.31	n.d	n.d
1-Methyl-2-propylbenzene	0.750	0.562	0.013	3.20	2.31	n.d	n.d
1,4-Dimethyl-2-ethylbenzene + 1,3-Dimethyl-4-ethylbenzene	-0.882	0.778	0.001	5.29	2.31	-20.6 ± 3.9 x 10 ⁻³	33.6 hr
1,2-Dimethyl-4-ethylbenzene	-0.957	0.915	0.000	9.30	2.31	-35.9 ± 3.9 x 10 ⁻³	19.30 hr
1,3-Dimethyl-2-ethylbenzene	-0.230	0.053	0.523	0.67	2.31	n.d	n.d
1,2-Dimethyl-3-ethylbenzene	-0.372	0.138	0.289	1.13	2.31	n.d	n.d

"continued..."

Table 5.3 "continued"

Compound	Statistical Analysis *					Rate Constant hr ⁻¹ (k _p ± S.E)	Half Life (t _{1/2}) ^b
	r	r ²	p	t _{cal}	t _{crit}		
1,2,4,5-Tetramethylbenzene + 1,2,3,5-Tetramethylbenzene	-0.979	0.959	0.000	13.70	2.31	-5.86 ± 0.43 x 10 ⁻²	11.82 hr
1,2,3,4-Tetramethylbenzene	-0.921	0.848	0.000	6.67	2.31	-2.14 ± 0.33 x 10 ⁻²	32.38 hr
Naphthalene	-0.984	0.967	0.000	15.40	2.31	-4.41 ± 0.29 x 10 ⁻²	15.7 hr
2-Methylnaphthalene	-0.993	0.986	0.000	22.20	2.36	-5.77 ± 0.26 x 10 ⁻²	12.01 hr
1-Methylnaphthalene	-0.980	0.961	0.000	13.20	2.36	-4.66 ± 0.35 x 10 ⁻²	14.9 hr
1+2-Ethylnaphthalene	-0.956	0.915	0.000	9.27	2.31	-4.35 ± 0.47 x 10 ⁻²	15.93 hr
2,6-Dimethylnaphthalene + 2,7-Dimethylnaphthalene	-0.531	0.282	0.142	1.70	2.36	n.d	n.d
1,3-Dimethylnaphthalene + 1,7-Dimethylnaphthalene	-0.856	0.732	0.003	4.40	2.36	-3.59 ± 0.82 x 10 ⁻²	19.30 hr
1,6-Dimethylnaphthalene	-0.974	0.948	0.000	10.50	2.45	-6.68 ± 0.64 x 10 ⁻²	10.37 hr
2,3-Dimethylnaphthalene + 1,4-Dimethylnaphthalene + 1,5-Dimethylnaphthalene	-0.943	0.889	0.000	7.50	2.36	-3.57 ± 0.48 x 10 ⁻²	19.41 hr

"continued..."

Table 5.3 "continued"

Compound	Statistical Analysis ^a					Rate Constant hr ⁻¹ (k _p ± S.E)	Half Life (t _{1/2}) ^b
	r	r ²	p	t _{cal}	t _{crit}		
1,2-Dimethylnaphthalene	-0.673	0.452	0.068	2.20	2.36	n.d	n.d
1,3,7-Trimethylnaphthalene	-0.859	0.738	0.028	3.36	2.78	-5.8 ± 1.7 x 10 ⁻²	11.95 hr
1,3,6-Trimethylnaphthalene	-0.274	0.075	0.599	0.57	2.78	n.d	n.d
1,3,5-Trimethylnaphthalene + 1,4,6-Trimethylnaphthalene	-0.439	0.192	0.325	1.10	2.57	n.d	n.d
2,3,6-Trimethylnaphthalene	-0.186	0.035	0.724	0.38	2.78	n.d	n.d
1,2,7-Trimethylnaphthalene + 1,6,7-Trimethylnaphthalene + 1,2,6-Trimethylnaphthalene	-0.646	0.418	0.166	1.69	2.78	n.d	n.d
1,2,4-Trimethylnaphthalene	-0.844	0.712	0.035	3.15	2.78	-5.61 ± 1.8 x 10 ⁻²	12.35 hr
1,2,5-Trimethylnaphthalene	----	----	----	----	----	n.d	n.d

^a r (Correlation coefficient), r² (Coefficient of determination), p (Significance level), |t| (Significant test: |t|_{cal} = Calculated value; |t|_{crit} = critical value, at 95% confidence interval) and S.E (Standard error of estimates), see also text.

^b 1 day under xenon lamp = 24 hr

n.d = not determined

dibenzothiophene and phenanthrene were not determined because their initial concentrations were too low to allow accurate measurements.

5.4.3 Statistical Analysis

To evaluate the significance of the outcome obtained for each SWSF compound, a scientific software packages (Fig.P Biosoft, Ferguson, MO 63135, U.S.A and Biosoft, 49 Baleman Street, Cambridge, CB2 1LR, U.K) was used to obtain a set of statistical parameters including the correlation coefficient (r), coefficient of determination (r^2), significance level (p), significance test (t) for a two-tailed test and standard error of estimates (SE) as given in Table 5.3. A brief description of the statistical terminology is given below.

The correlation coefficient (r): is a measure of the linear association between two variables, in this case concentration versus irradiation time. It is an indication of the goodness of fit of a regression. It must lie between -1 and +1; if two variables are highly positively correlated, the value of r would be towards the top end of the range (i.e +1); if the variables were highly negatively correlated, where one exerts a strong inverse influence on the other, the value of r would tend towards -1. If r tended towards zero, it would mean an absence of linear correlation (Miller and Miller, 1988).

Coefficient of determination (r^2): is a measure of the extent to which the variation in one variable (i.e. concentration) may be accounted for by the variation in another variable (i.e. time of irradiation).

Significance level (p): provides a statistical method of determining the validity of

correlating concentration with time of irradiation. Only those differences which appear significant at $p=0.05$ (5%) or less are considered.

Significance test (t): In making a significance test, the truth of a hypothesis, known as the Null Hypothesis (H_0), is tested. In the present case, we test the Null Hypothesis that the best slope of a SWSF is statistically equal to 0 against the alternative hypothesis that it is not equal to 0. If the calculated value of $|t|$ without regard to sign exceeds a certain critical value then the Null Hypothesis is rejected. The critical value of $|t|$ for a particular significance level is found from the t-distribution table (see Miller and Miller, 1988).

Standard Error of estimates (SE): measures the scatter of the points about the regression line of Y (i.e. concentration) on X (i.e. irradiation time) and provides an indication of the variation contained in the data.

5.4.4 Benzene and Alkylbenzenes

A first order photodegradation rate was not exhibited by either benzene or toluene (Figure 5.2) and an absence of linear correlation was found ($r^2 = 2\%$ and 1% respectively).

The C_2 alkylbenzenes (Figure 5.3) and C_3 alkylbenzenes (Figure 5.4) also showed no significant degradation up to 48 hours under the xenon lamp. Although 1,2,4- and 1,2,3-trimethylbenzenes possessed higher r^2 value (20% and 22% respectively) compared to other C_3 alkylbenzenes ($\leq 1\%$), the $|t|$ value of the slopes were less than the critical value, hence any photodegradation was not statistically reliable (Table 5.3).

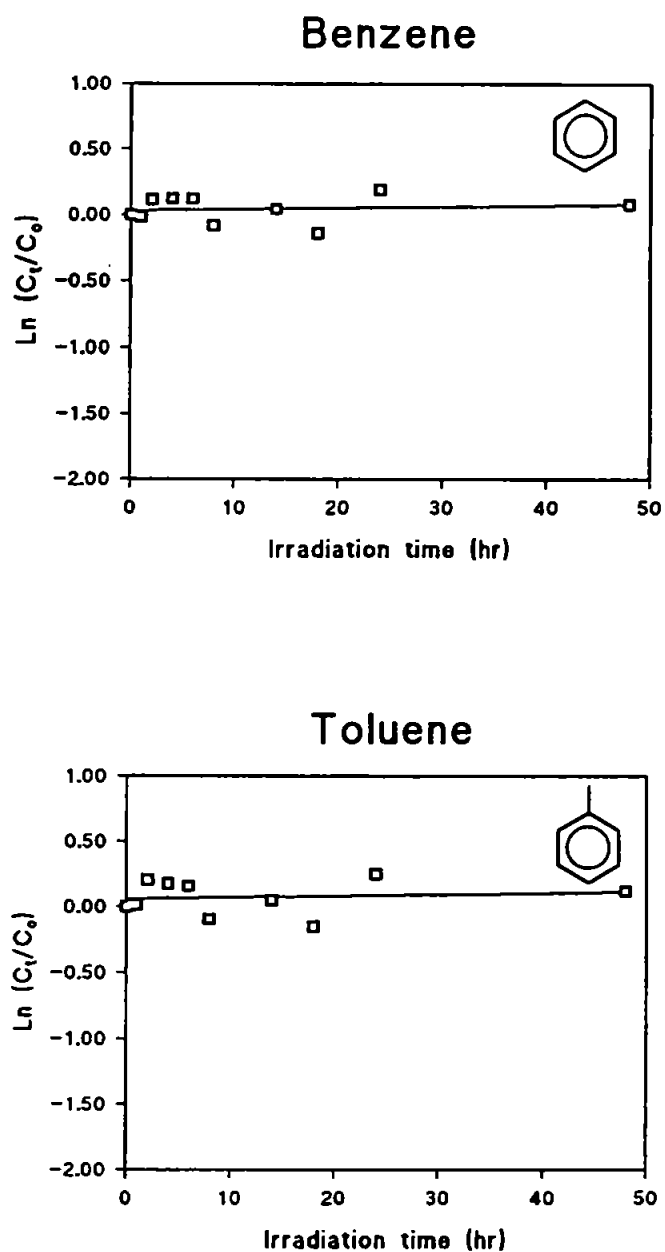


Figure 5.2 Plots of the photochemical fate of benzene and toluene with respect to time of irradiation under the xenon lamp.

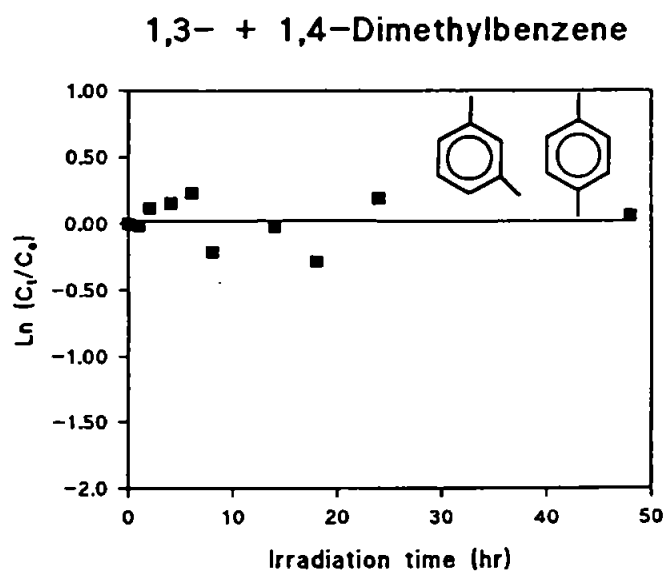
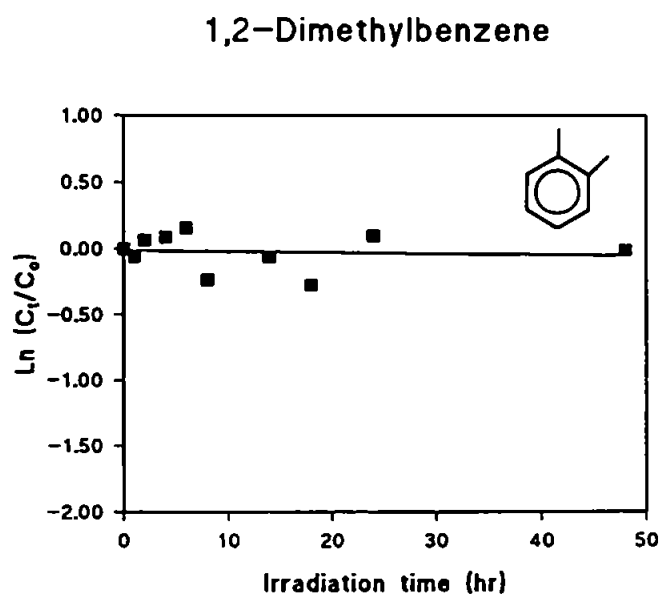
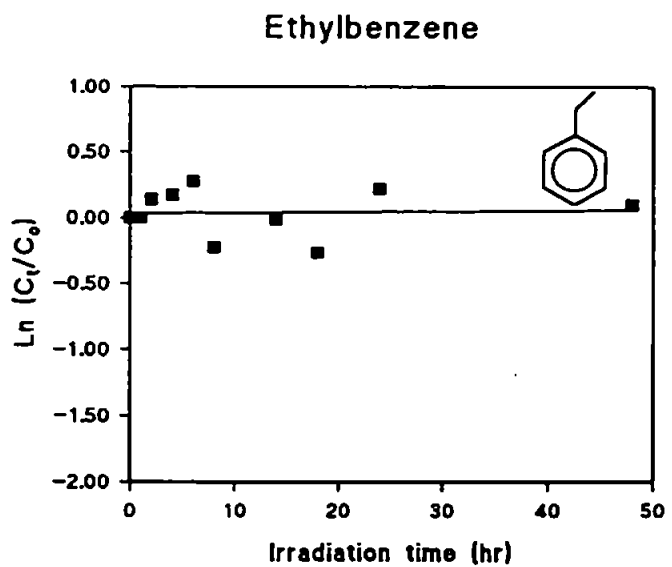


Figure 5.3 Plots of the photochemical fate of C_2 alkylbenzenes with respect to time of irradiation under the xenon lamp.

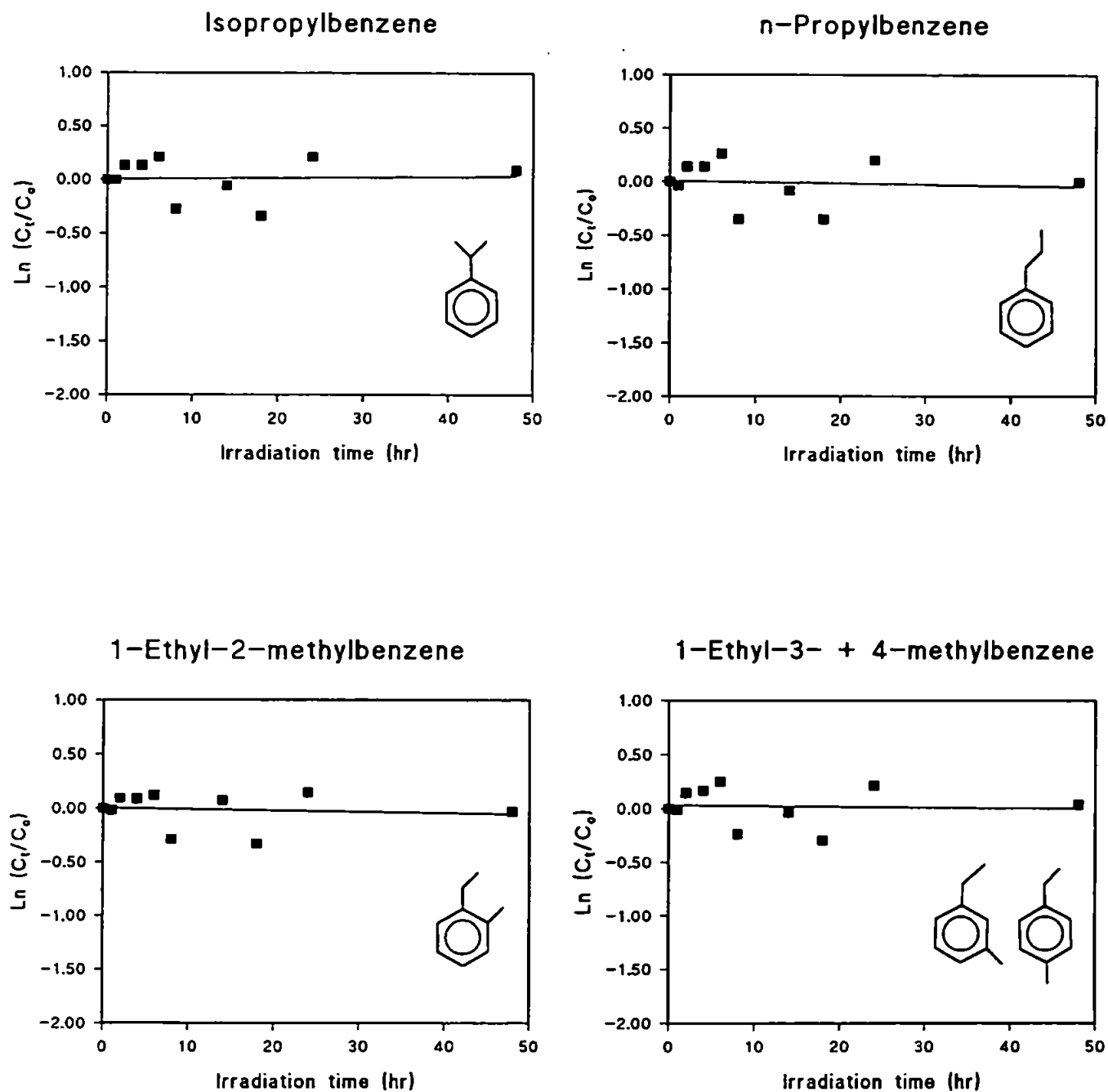


Figure 5.4 Plots of the photochemical fate of C_3 alkylbenzenes with respect to time of irradiation under the xenon lamp.

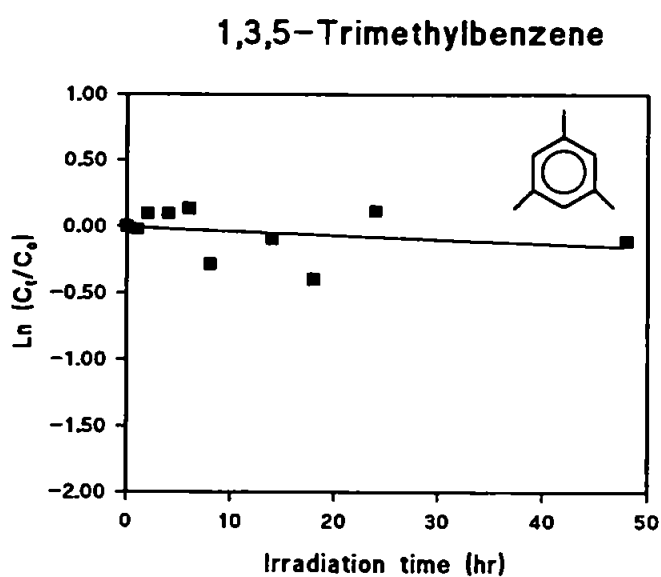
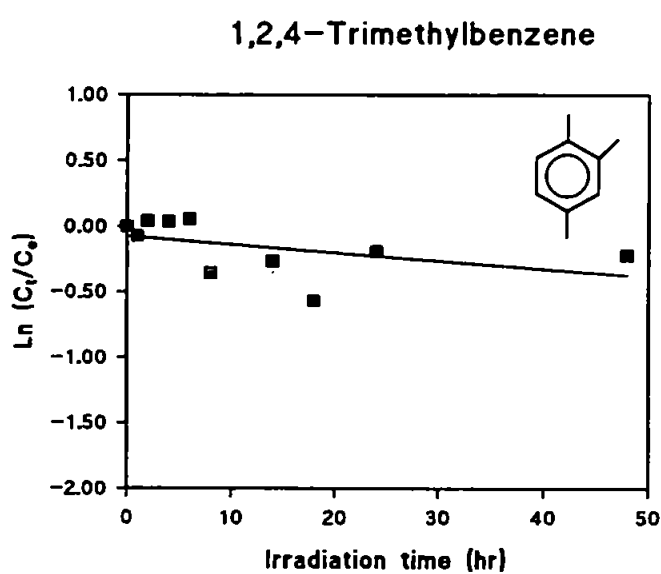
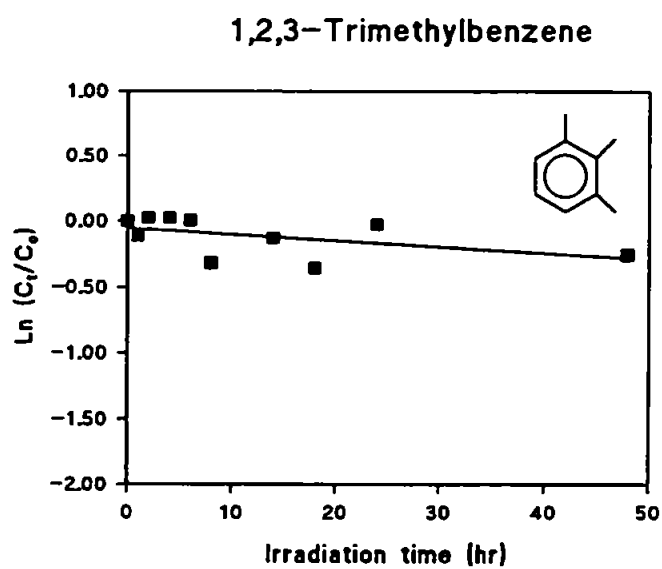


Figure 5.4 "Continued"

Although the recovery of these highly volatile SWSF components was good and showed close agreement between the experiments conducted in Chapter 3 and in this study, the small variations evident on the graphs (Figure 5.2 - 5.4) are covariant with benzene and toluene and most probably arise from variations in sample volumes, adsorption or any volatile losses which may have occurred during the analytical procedure.

These results are entirely as expected. Benzene does not absorb light at wavelengths beyond 269 nm (Ranby and Rabek, 1975). Similarly alkylbenzenes from C₁-C₄ which were also present in the SWSF, do not absorb at wavelengths > 300 nm. Therefore direct photodegradation (i.e. direct absorption of radiation by a compound) due to natural sunlight is unlikely.

However, natural seawater often contains significant concentrations of photosensitizing components such as humic substances (Zepp *et al.*, 1985; Zepp, 1988) and carbonyl compounds (Mopper and Stahovec, 1986) which are capable of participating in the degradation mechanisms of aquatic pollutants. Anthraquinone is one of the photosensitizing carbonyl compounds which has been detected in seawater at a range of concentrations from 10⁻⁹-10⁻¹¹ g L⁻¹ (Ehrhardt *et al.*, 1982). Ehrhardt and Petrick (1984) showed that anthraquinone assisted the photooxidation of ethylbenzene and other homologous short-chain mono-alkylated benzenes in conjunction with natural and artificial sunlight. It was found that anthraquinone reacted via its excited first triplet state to abstract a benzylic hydrogen atom from the alkylbenzene and thereby initiate a chain reaction with stable aldehyde, ketone and alcohol end products (details of the reaction mechanism were given in the summary of some photodegradation studies recorded in the preceding chapter).

The other route by which ethylbenzene could be photooxidized is via molecular singlet

oxygen $^1\text{O}_2$, as discussed in Chapter 4, which could be formed by energy transfer from the first triplet state of anthraquinone to ground state triplet oxygen $^3\text{O}_2$. However, Ehrhardt and Petrick (1984) believed that singlet oxygen does not carry sufficient energy (94 Kcal mole⁻¹) to attack the benzylic position of alkylbenzenes.

No photodegradation of the C₁-C₃ alkylbenzenes was observed by either of these pathways in the study undertaken here. Assuming that anthraquinone or similar photosensitisers were present in the natural seawater used, then it may be that the excited photo-sensitizer (i.e. anthraquinone) had been quenched by other substances such as oxygen, which is an efficient triplet quencher in seawater (Zika, 1981).

It is of interest to compare the stability of toluene and the dimethylbenzenes in the seawater solution irradiated by the xenon lamp in this study with other reports. Neat samples of these substrates were observed to give several oxidation products after irradiation with pyrex-filtered light ($\lambda > 285$) from a mercury lamp between 24-96 hr in the presence of oxygen (Sydnes *et al.*, 1985a). This shows that either the mercury lamp, which has a higher radiation energy at the absorption wavelengths of these compounds than the xenon lamp, permits the cleavage of the benzylic C-H bond, or that oxygen is an important part of the degradation pathway. The latter may be of more significance since Sydnes *et al.* (1985a) demonstrated that deoxygenated toluene and dimethylbenzenes yielded no photooxidation products. The photooxidation was found to occur over a charge transfer complex (CTC) of toluene (or dimethylbenzene) with molecular oxygen. The formation of a CTC complex shifts the light absorption to higher wavelengths thus facilitating the formation of hydroperoxide as mentioned in the previous chapter, 4.1.2. Ranby and Rabek (1975) mentioned for instance that the CTC complexes of benzene and oxygen increases the absorption of benzene up to 340 nm.

Unfortunately, it was not possible to speculate whether the presence of oxygen could account for the lack of detectable breakdown of toluene, dimethylbenzenes and other alkylbenzenes in this study, because the content of oxygen in SWSF solution before irradiation was not measured. It is possible that the available oxygen was consumed by other SWSF compounds which have the ability to undergo direct photooxidation faster and which then use up the oxygen. This was found to occur in the case of phenanthrene for example (Chapter 4).

However, it must be mentioned that the photoirradiation of toluene and methylbenzenes as neat samples as carried out by Sydnes *et al.* (1985a) deviate from those of the natural environment. Mill (1980) also mentioned that photoreaction rates differ in water solution as compared with organic solvents. For instance, the life time of singlet oxygen in an organic solvent is considerably longer than in water allowing more scope for the reaction between singlet oxygen and a compound to proceed. Furthermore, Zepp *et al.* (1977) reported that photoreactions are sometimes concentration dependent and are therefore more likely to yield different products when the concentrations of the reactants varies.

Among all 18 isomers of the C₄ benzenes that were irradiated within the SWSF, only 7 showed evidence of first order degradation (Figure 5.5). However, because of the co-elution of some of these isomers as one peak in the chromatographic analysis, it was not possible to determine which of the individual components contributed to the calculated $t_{1/2}$. The absorption of these compounds just within the wavelength emitted by the xenon lamp (approximately 290 nm; Heraeus GmbH, Heraeus Equipment Ltd., U.K) may have facilitated their degradation. This is in agreement with the observations of Klein and Pilpel (1974b) who found that *sec*-butylbenzene was degraded when irradiated with UV from a filtered mercury lamp > 290 nm.

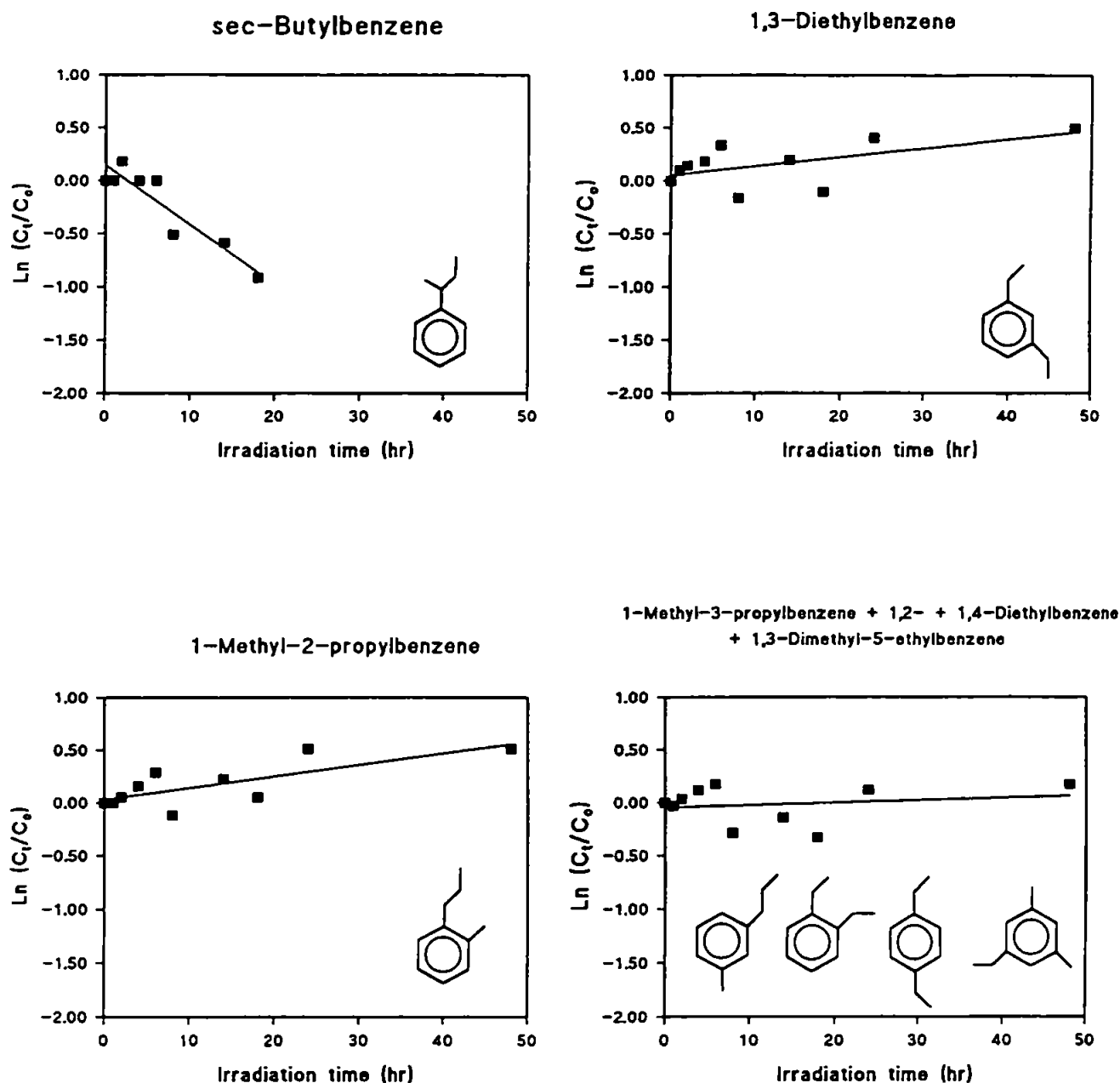


Figure 5.5 Plots of the photochemical fate of C_4 alkylbenzenes with respect to time of irradiation under the xenon lamp.

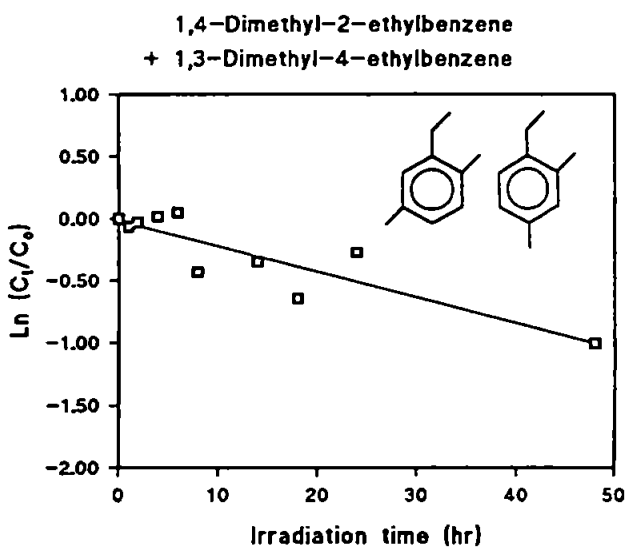
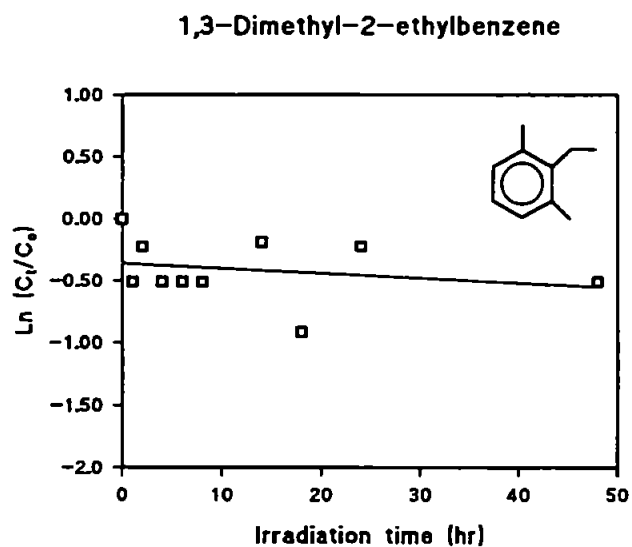
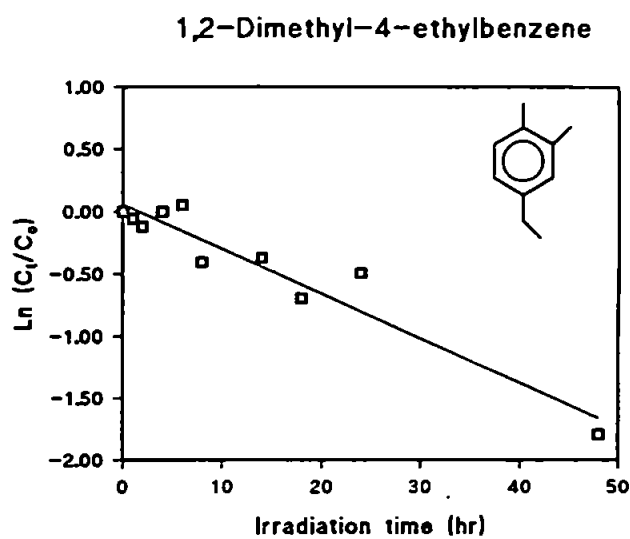
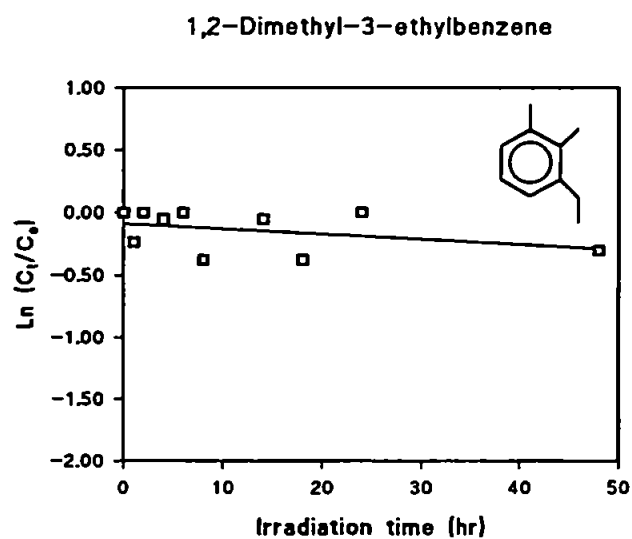


Figure 5.5 "Continued"

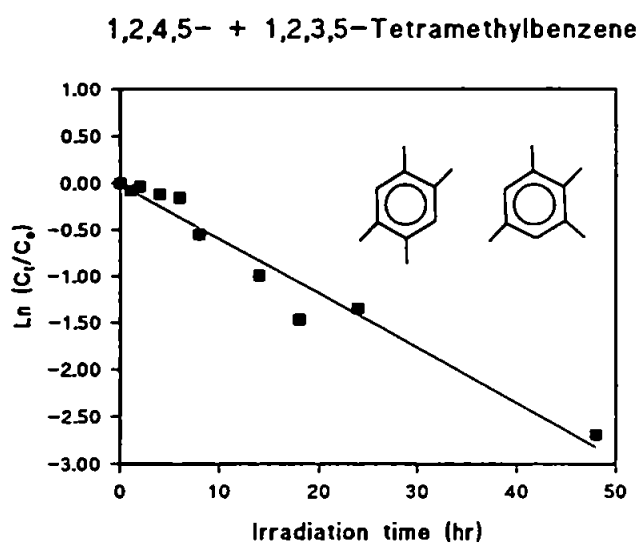
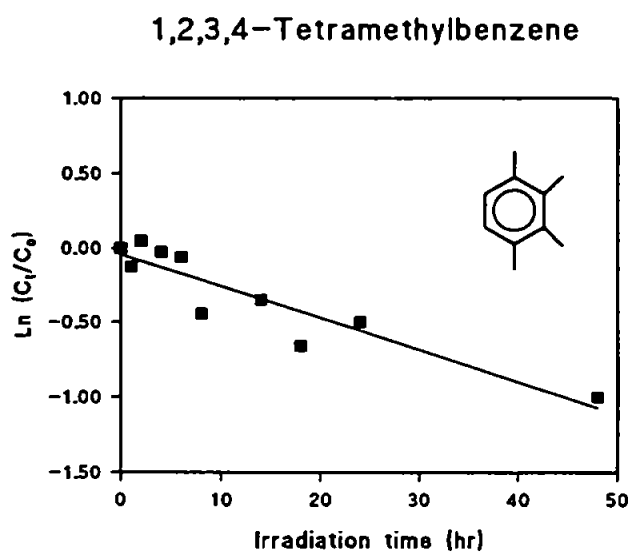
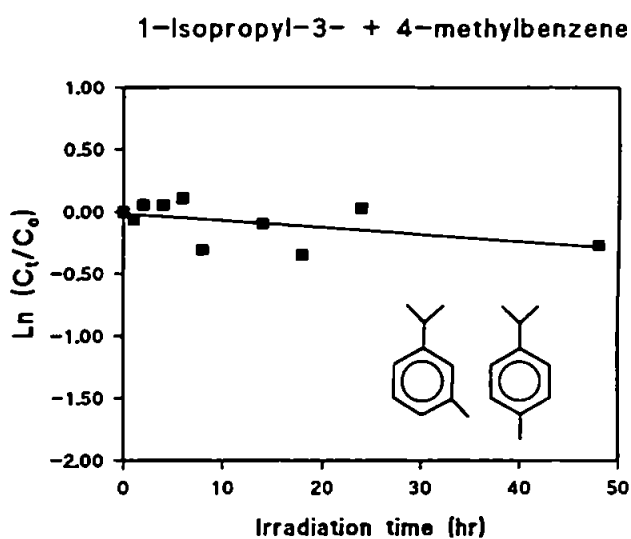
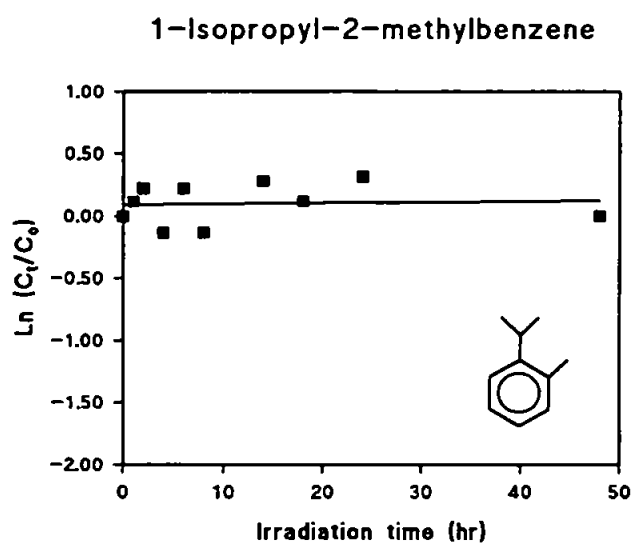


Figure 5.5 "Continued"

The time-course study of these isomers showed that the half life of *sec*-butylbenzene was 12.3 hr, 1,2-dimethyl-4-ethyl benzene 19.30 hr, and 1,4-dimethyl-2-ethylbenzene + 1,3-dimethyl-4-ethylbenzene (one peak) 33.6 hr. On the other hand while 1,2,4,5- + 1,2,3,5-tetramethylbenzene (one peak) had $t_{1/2}$ of 11.8 hr, more than double this time was required for degradation of 1,2,3,4-tetramethylbenzene (32.4 hr) (Table 5.3). The $t_{1/2}$ of the above isomers were calculated from their slopes obtained from the regression line within the 95% confidence limits.

To examine the statistical significance of differences between the $t_{1/2}$ of the different isomers, a comparison was made between *sec*-butylbenzene, 1,2-dimethyl-4-ethylbenzene and 1,2,3,4-tetramethylbenzene which eluted as separated peaks. The standard error (\pm SE) was applied at the 95% confidence intervals on the slope of each isomer (i.e $k_p \pm$ SE). This would give a range of variability of the slope (k_p) value and determine whether the slopes lie in the same range.

The ranges of the slopes of the three isomers were as follows:

$$1,2,3,4\text{-tetramethylbenzene } (k_p \pm \text{SE}) = (-0.018) - (-0.025)$$

$$1,2\text{-dimethyl-4-ethylbenzene } (k_p \pm \text{SE}) = (-0.040) - (-0.032)$$

$$\textit{sec}\text{-butylbenzene } (k_p \pm \text{SE}) = (-0.047) - (-0.065)$$

These results are also displayed in Figure 5.6. As can be seen from the derived values and the graph, the slopes of these three isomers lie in different ranges. This means that the k_p of each isomer is not the same.

The finding that certain isomers have a faster degradation rate than others could be related to the pattern of substitution i.e the position of substitution on the benzene ring and perhaps the type of substitution as well. For example, the degradation of 1,2-dimethyl-4-

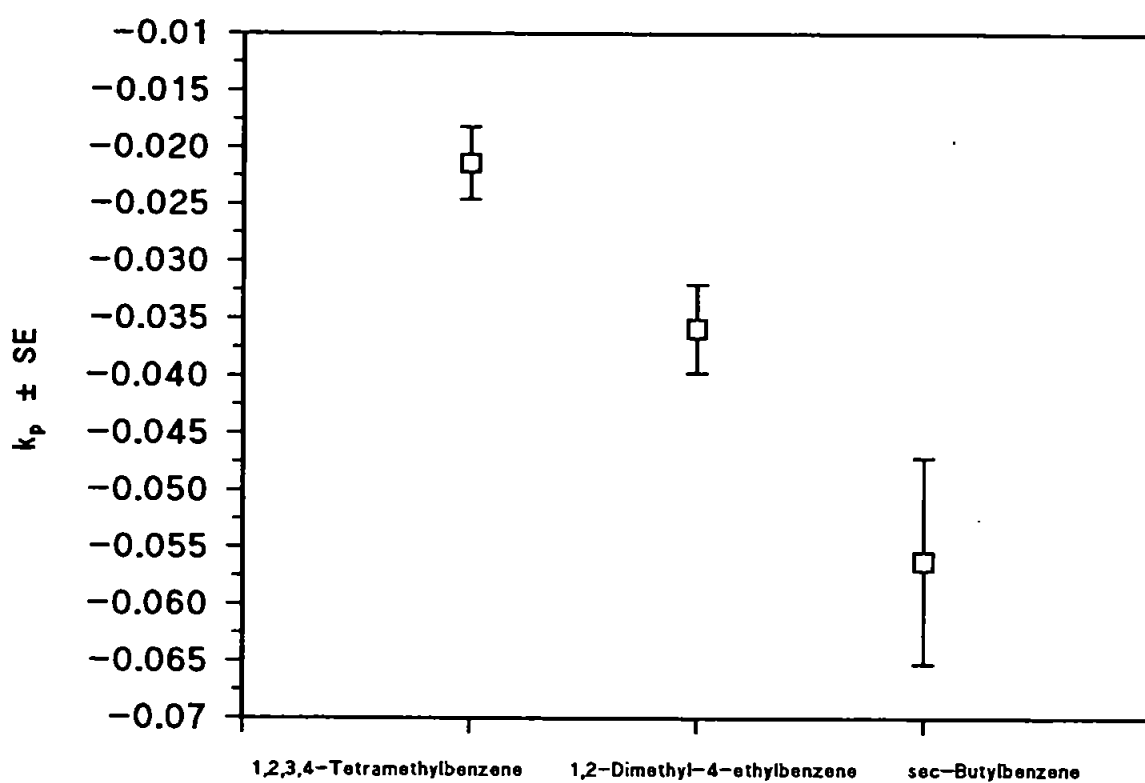


Figure 5.6 Photodegradation rate constant ($k_p \pm SE$) of C₄ alkylbenzene isomers at 95% confidence interval.

ethylbenzene was faster than the degradation of 1,4-dimethyl-2-ethylbenzene + 1,3-dimethyl-4-ethylbenzene which may have been facilitated by the *ortho*-proximity of the two methyl groups on the ring (Sydnes *et al.*, 1985a). The photodegradation of *sec*-butylbenzene was even faster and could be ascribed to the presence of a reactive tertiary hydrogen atom in the side chain of this isomer (Klein and Pilpel, 1974b).

Although photodegradation half-lives of all of these benzenes were < 35 hr under the xenon lamp, their differing susceptibilities to photodegradation could have important environmental implications, particularly with respect to the toxicity of the breakdown products in the marine environment (Sydnes and Burkow, 1985). These findings accentuate the importance of an isomer-specific study such as that conducted here. An examination of the literature relating to oil degradation revealed that very few isomer-specific photolysis studies of alkylaromatic compounds have previously been carried out.

5.4.5 Naphthalene and Alkylnaphthalenes

The majority of the naphthalenes (i.e C₀-C₃) identified in the SWSF of Kuwait crude oil exhibited first order photodegradation rate constant (Figure 5.7 - 5.9). Some apparently did not, (e.g 1,3,6-, 2,3,6-trimethylnaphthalene) but this may have been due to initial low concentrations which meant that levels fell below detection limits after only a short period of irradiation (Table 5.1). The high absorption coefficient of these compounds at wavelengths 280-320 nm (UV-B) probably facilitated the photodegradation under the irradiation conditions employed.

The photodegradation rate constant (k_p) of naphthalene was 0.044 hr⁻¹ ($r^2 = 95\%$, $p = 0.000$) and the calculated $t_{1/2}$ was found to be 15.7 hr (Table 5.3). Fukuda *et al.* (1988)

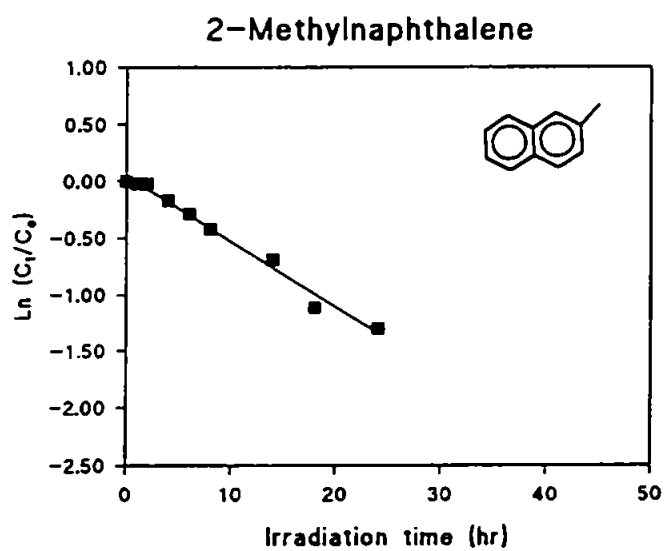
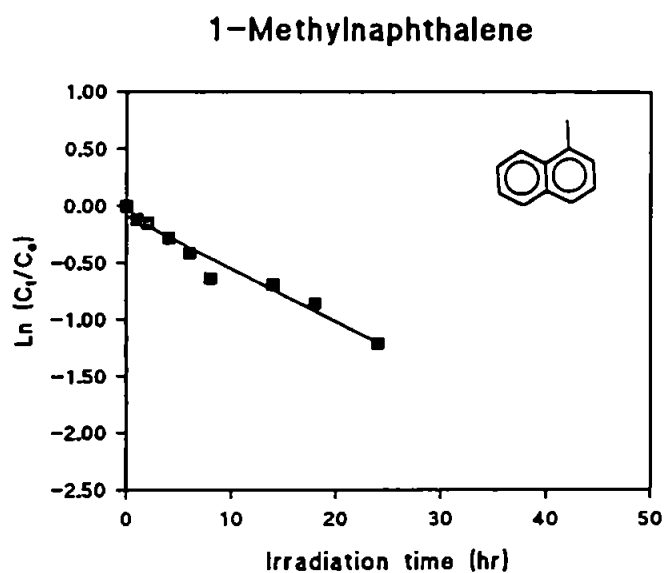
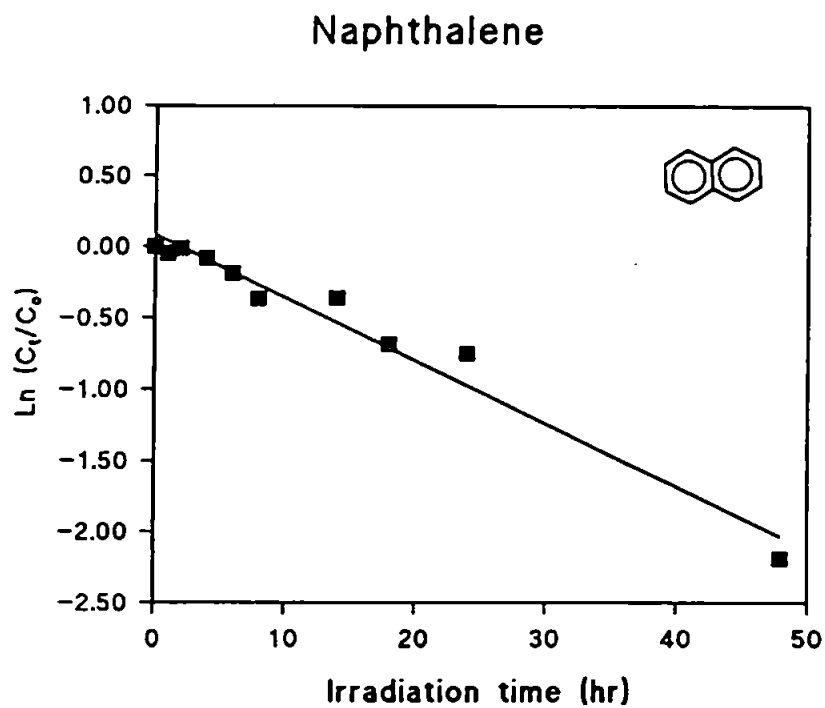


Figure 5.7 Plots of the photochemical fate of naphthalene and methylnaphthalenes with respect to time of irradiation under the xenon lamp.

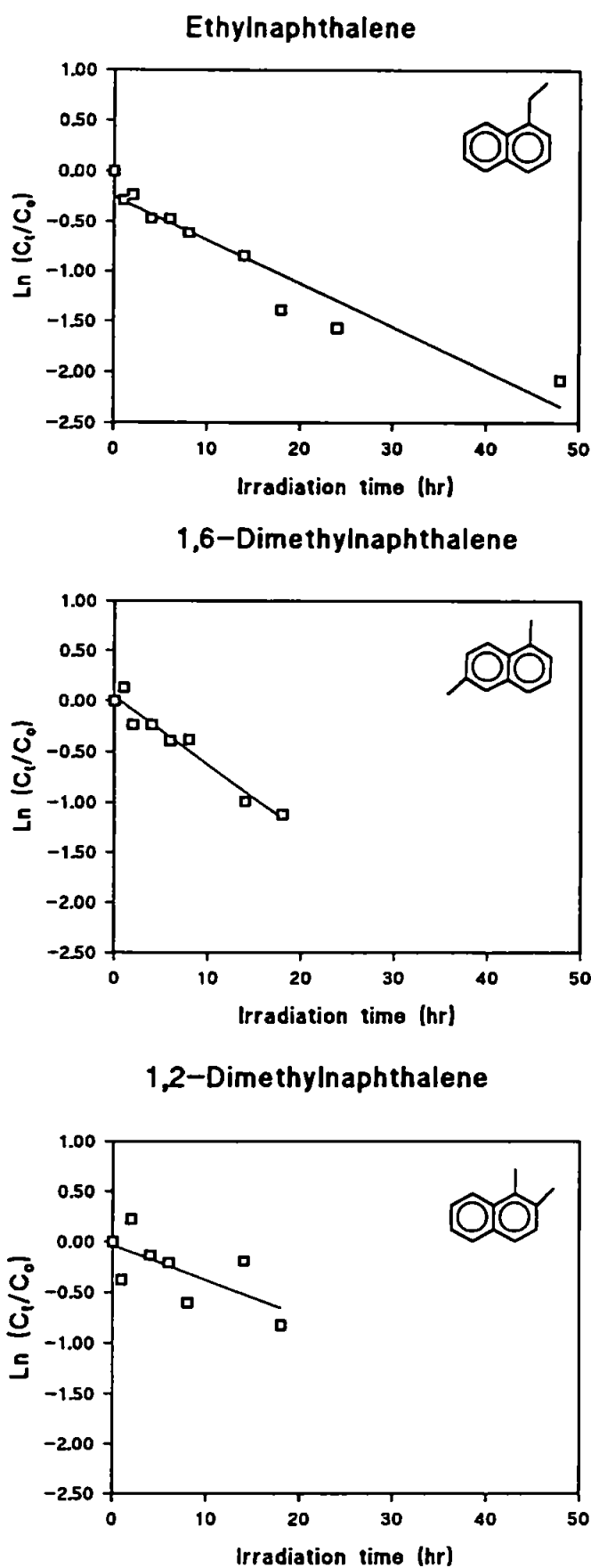
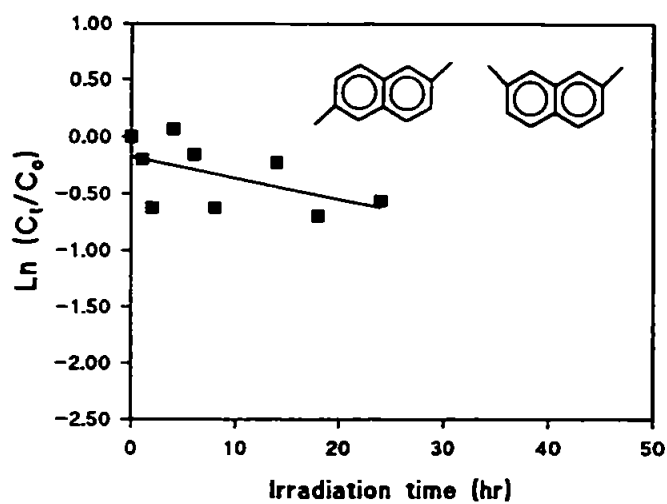
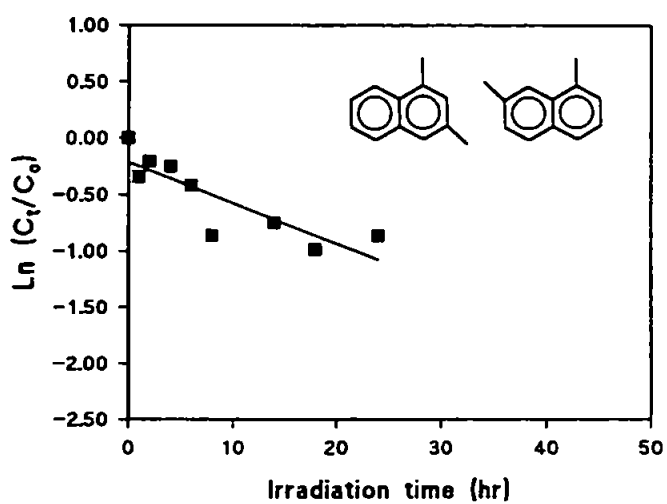


Figure 5.8 Plots of the photochemical fate of C_2 alkyl naphthalenes with respect to time of irradiation under the xenon lamp.

2,6-Dimethylnaphthalene + 2,7-Dimethylnaphthalene



1,3-Dimethylnaphthalene + 1,7-Dimethylnaphthalene



1,4-Dimethylnaphthalene + 2,3-Dimethylnaphthalene + 1,5-Trimethylnaphthalene

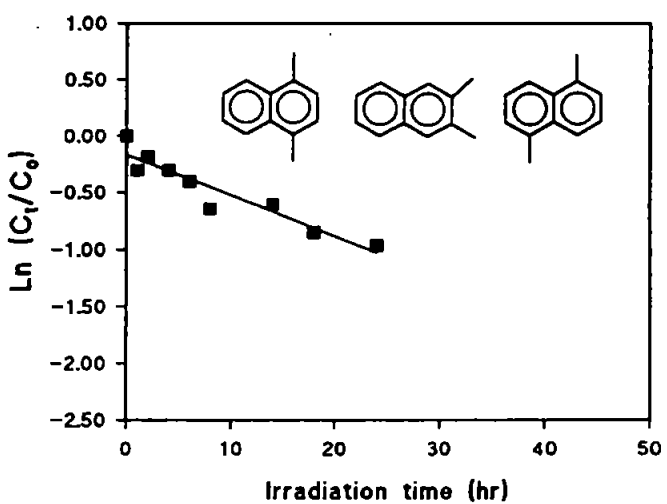
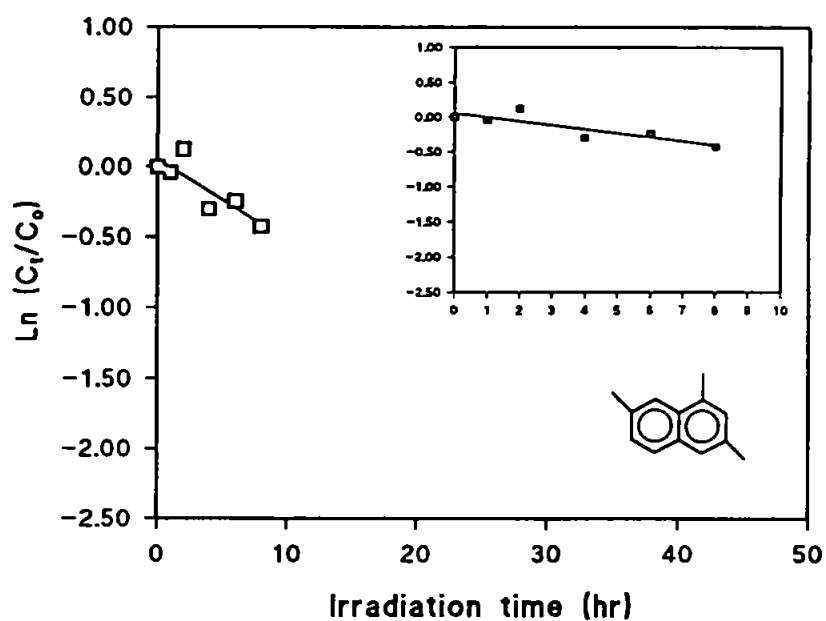


Figure 5.8 "Continued"

1,3,7-Trimethylnaphthalene



1,3,6-Trimethylnaphthalene

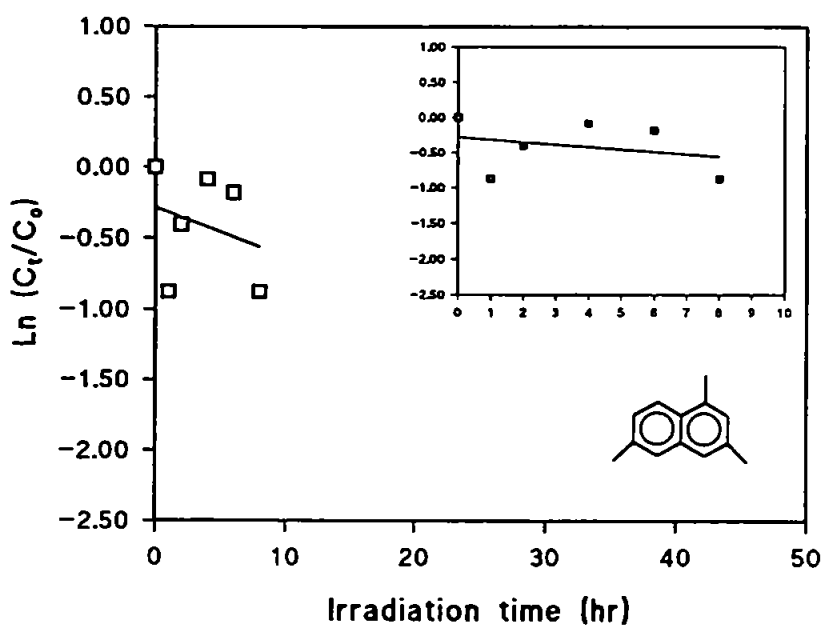


Figure 5.9 Plots of the photochemical fate of trimethylnaphthalenes with respect to time of irradiation under the xenon lamp.

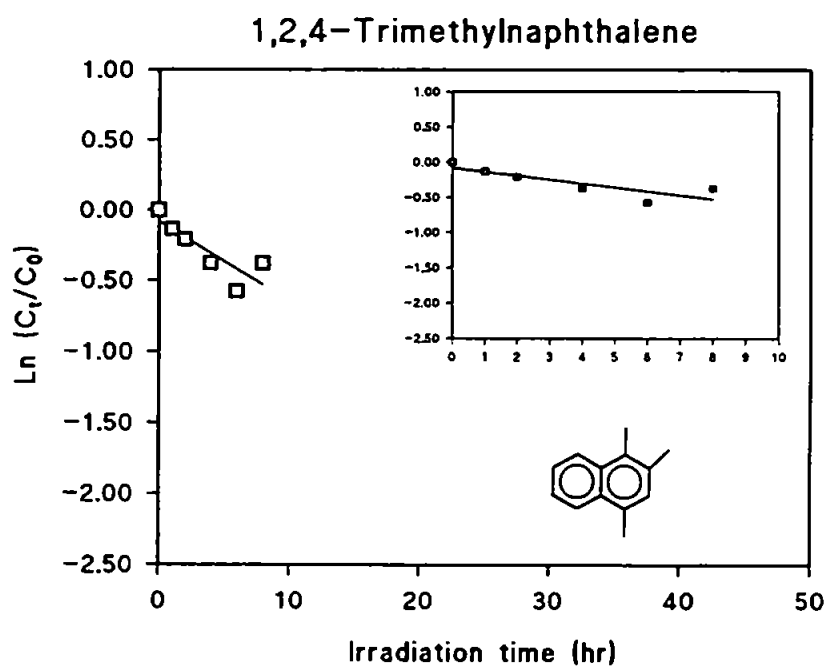
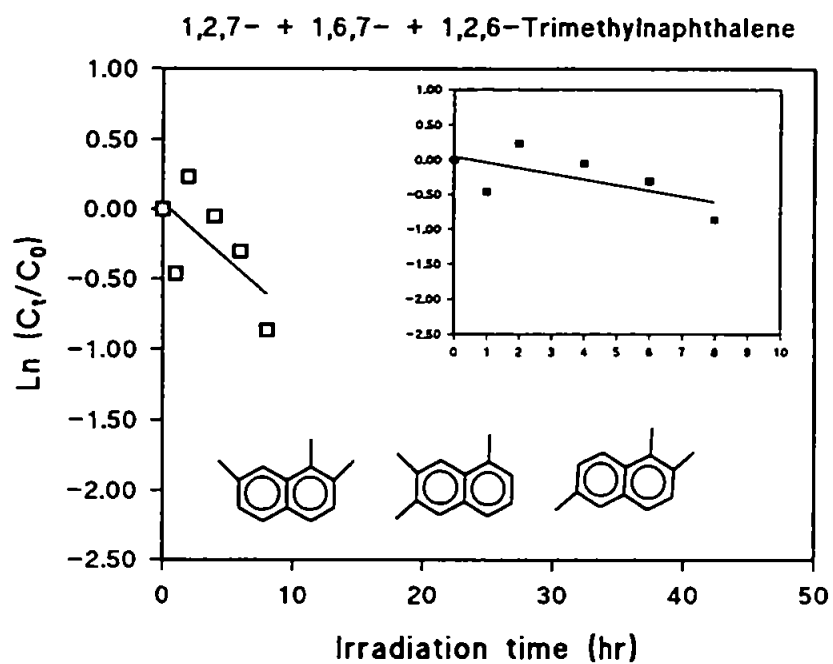
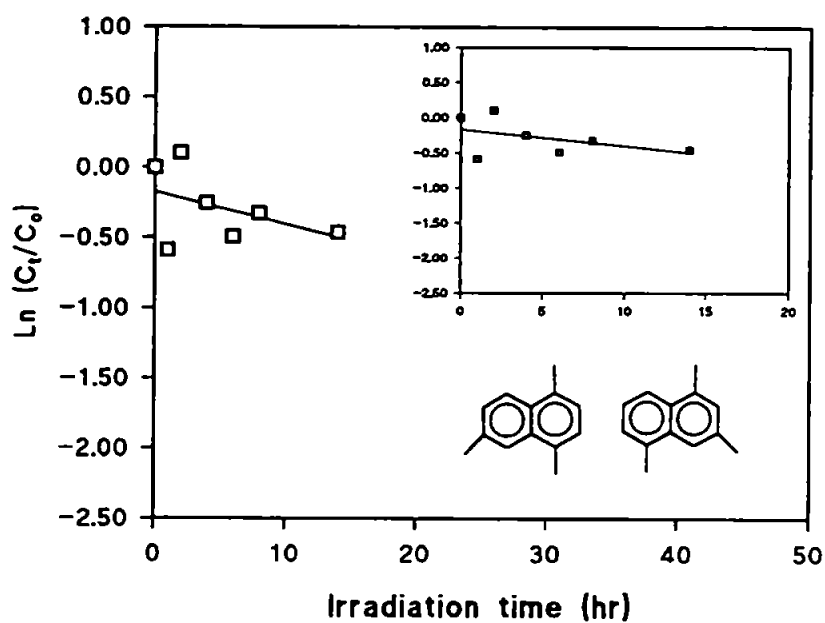


Figure 5.9 "Continued"

1,4,6-Trimethylnaphthalene + 1,3,5-Trimethylnaphthalene



2,3,6-Trimethylnaphthalene

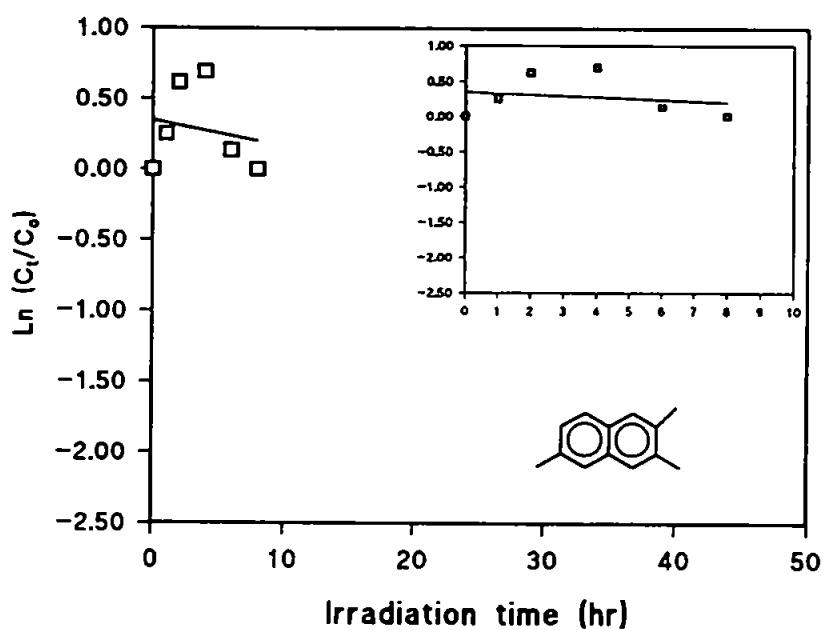


Figure 5.9 "Continued"

reported a slower photodegradation rate (0.028 hr^{-1}) and half life for naphthalene (25 hr) using a high pressure mercury lamp to study naphthalene solutions in distilled water at $25 \pm 1 \text{ }^{\circ}\text{C}$. These authors reported that the photolysis rate increased several times in artificial seawater and in proportion to the salt concentration, but no precise values were reported until now.

The 1-methyl- and the 2-methylnaphthalene degradation rate constants were higher than that of naphthalene (4.7 hr^{-1} , $r^2 = 99\%$ and 5.8 hr^{-1} , $r^2 = 96\%$, $p = 0.000$, respectively), hence their $t_{1/2}$ were shorter (14.9 and 12 hr respectively, Table 5.3).

The finding that methylnaphthalenes photodegraded more rapidly than naphthalene was more clearly demonstrated by calculating the ratio of compounds as a function of irradiation time (see Table 5.1; Figure 5.10). Similar findings have been reported by Ehrhardt *et al.* (1992) for naphthalene as well as for methylfluorenes to fluorene, methyldibenzofurans to dibenzofuran and methylphenanthrene to phenanthrene. The rapid degradation of the methylnaphthalene derivatives mentioned can be explained by the presence of the alkyl side chain. Light induced side chain fragmentation and oxidation at the benzyl position of the methyl substituted aromatics has been previously demonstrated for alkylbenzenes by Ehrhardt and Petrick (1984) and Rontani *et al.* (1987).

The $t_{1/2}$ of the two methyl isomers revealed that the 2-methylnaphthalene photodegraded faster than 1-methylnaphthalene (Figure 5.7). Comparison of the $k_p \pm \text{SE}$ values for the two isomers [1-methyl-: (-0.043) - (-0.050); 2-methyl- (-0.055) - (-0.060)], showed that their slopes lie in different ranges and thus the difference is statistically significant ($p=0.00$). It is not clear why 2-methylnaphthalene reacts faster than 1-methylnaphthalene. However, as suggested by Sydnes *et al.* (1985b) photooxidation of alkylnaphthalene may

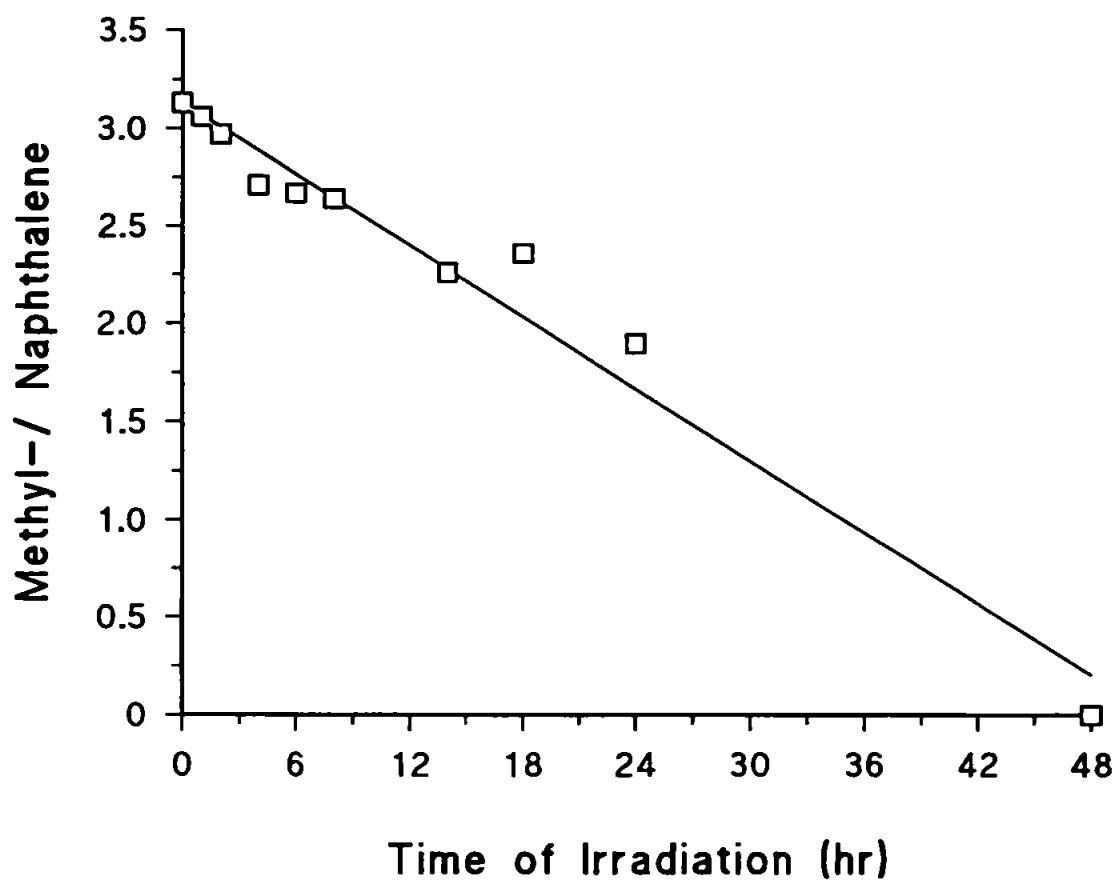


Figure 5.10 Ratios of methylnaphthalene / naphthalene in the irradiated SWSF as a function of time.

occur by oxidation of the methyl group. If that were so then it is possible that the *peri* strain effect of the 1-methylnaphthalene makes the methyl group a crowded position for oxygen to attack and more difficult for the abstraction of the benzylic hydrogen compared to the uncrowded alkyl position of the 2-methylnaphthalene.

The half life reported by Fukuda *et al.* (1988) for 2-methylnaphthalene of 16.4 hr under a high pressure mercury lamp and in distilled water, was relatively close to the 12 hr half life found in this study. In addition, this $t_{1/2}$ was found to be less in artificial seawater as shown for naphthalene.

1+2-ethylnaphthalene possessed a $t_{1/2}$ of 15.9 hr which was very close to that of naphthalene (15.7 hr) even though the two compounds had different initial concentrations. The calculated $t_{1/2}$ of 1,2-dimethylnaphthalene was 19.9 hr, although the statistical analysis of the slope showed that this was not well correlated with irradiation time. The r^2 was only 45% with p value $> 5\%$, i.e. only 45% of the variation in concentration can be explained by variation in irradiation time. Similarly for 2,6+ 2,7-dimethylnaphthalene, r^2 was 28%, $p > 5\%$ where only 28% of the variation in concentration can be attributed to variation in irradiation time. The scattering of the data was too great to allow determination of accurate photodegradation rate constants k_p (see Figure 5.8).

The photodegradation regression of 1,6-dimethylnaphthalene was significant, r^2 was 95% at $p = 0.000$, and the calculated $t_{1/2}$ from the slope was 10.4 hr. 1,6-dimethylnaphthalene is more rapidly photodegraded than 1+2-ethylnaphthalene and even faster than 2-methyl and 1-methylnaphthalene (Table 5.3). The availability of two benzyl positions in the di-substituted alkyl compound could explain this higher photodegradability when compared with only one reactive position in the case of the isomers mentioned above. The other

dimethylnaphthalenes, which also showed a significant degradation regression, co-eluted as a single peak which did not allow the determination of the degradation rates for the individual isomers. The differing reactivity of the dimethylnaphthalene isomers was also reported by Sydnès *et al.* (1985b) and was characterized by the differing products and product yields following irradiation.

Sydnès *et al.* (1985b), suggested that photooxidation of dimethylnaphthalenes can occur by different mechanisms depending on the irradiation conditions. Direct oxidation can occur at the benzylic position although not efficiently, but, in the presence of a singlet oxygen sensitizer such as oil or methylene blue, Diels-Alder addition predominates over methyl group oxidation. The characterisation of the photoproducts may allow the elucidation of the particular mechanism responsible for the degradation encountered as demonstrated for phenanthrene in the previous chapter. This was outside the scope of the present study in the time available.

Among the 10 trimethylnaphthalene isomers which were irradiated, (**Figure 5.9**), 1,3,7- and 1,2,4-trimethylnaphthalenes had the highest r^2 (74% and 71% respectively both at $p < 5\%$, **Table 5.3**). The calculated $t_{1/2}$ were also similar (11.95 hr and 12.35 hr respectively) which suggested that the two isomers might share some similarity in their photodegradation. However, the significance of the regression might have been affected by the lower number of determinations of these two isomers ($n=6$) with irradiation time as compared to other compounds.

For the rest of the trimethylnaphthalene the scattering of the data as shown in **Figure 5.9**, which was a consequence of the low initial concentrations of these compounds, affected the accuracy of the integrated peak areas and consequently the k_p value and the calculated

half lives (Table 5.3). Use of larger volumes for photolysis would be more reliable, particularly for compounds which possess a low water solubility, such as C₃ alkyl naphthalenes.

A summary of the SWSF compounds which were significantly photodegraded is given in Table 5.4. According to Zepp and Schlotzhauer (1979) there is a ragged trend of increasing photoreactivity with increasing molecular weight of aromatic hydrocarbons and the opposite is the case for microbial oxidation. However, in the present study, it appears that within one group of isomers there are differences in photodegradation rates which are not accounted for by the above statement. Having said that, the photodegradation rates of the naphthalenes (apart from C₂-alkyl naphthalenes) did show that photodegradation of C₃ alkyl naphthalenes is faster than C₁ than C₀ alkyl naphthalenes and even better agreement is demonstrated when the t_{1/2} determined for phenanthrene (2-2.2 hr, see Chapter 4) is compared with that of naphthalene (15.7 hr) under the xenon lamp. This sequence is the reverse of the expected seawater solubility of these chemicals (McAuliffe, 1966).

5.4.6 Estimation of the Expected Half-Lives of the SWSF Under Sunlight

In order to relate the rate of degradation caused by the xenon lamp to the rate likely to occur in sunlight at specific latitude L and season S, Parker and Leahey (1988) derived a conversion equation which can be used to estimate the rate of photodegradation which may occur at latitudes from 20 to 50 °N as mentioned in the previous chapter (4.4.2). According to the equation, the amount of light intensity from the xenon lamp relative to Florida midday, midsummer (Latitude 25-35 °N) is:

Assuming 12 hr of daylight,

Table 5.4 Summary of the significant photodegraded SWSF compounds irradiated under xenon lamp at 25 °C.

Compound	$k_p \pm \text{SE (hr}^{-1}\text{)}$	$t_{1/2} \text{ (hr)}$
Benzenes		
<i>sec</i> -Butylbenzene	$-56.2 \pm 9.1 \times 10^{-3}$	12.3
1,4-Dimethyl-2-ethylbenzene + 1,3-Dimethyl-4-ethylbenzene	$-20.6 \pm 3.9 \times 10^{-3}$	33.6
1,2-Dimethyl-4-ethylbenzene	$-35.9 \pm 3.9 \times 10^{-3}$	19.3
1,2,4,5-Tetramethylbenzene + 1,2,3,5-Tetramethylbenzene	$-5.86 \pm 4.3 \times 10^{-3}$	11.8
1,2,3,4-Tetramethylbenzene	$-2.14 \pm 0.32 \times 10^{-2}$	32.4
Naphthalenes		
Naphthalene	$-4.41 \pm 0.29 \times 10^{-2}$	15.7
2-Methylnaphthalene	$-5.77 \pm 0.26 \times 10^{-2}$	12.0
1-Methylnaphthalene	$-4.66 \pm 0.35 \times 10^{-2}$	14.9
1+2-Ethylnaphthalene	$-4.35 \pm 0.47 \times 10^{-2}$	15.9
1,3-Dimethylnaphthalene + 1,7-Dimethylnaphthalene	$-3.59 \pm 0.82 \times 10^{-2}$	19.3
1,6-Dimethylnaphthalene	$-6.68 \pm 0.64 \times 10^{-2}$	10.4
2,3-Dimethylnaphthalene + 1,4-Dimethylnaphthalene + 1,5-Dimethylnaphthalene	$-3.57 \pm 0.48 \times 10^{-2}$	19.4
1,3,7-Trimethylnaphthalene	$-5.8 \pm 1.7 \times 10^{-2}$	12.0
1,2,4-Trimethylnaphthalene	$-5.61 \pm 1.8 \times 10^{-2}$	12.4

2.78 hr under the xenon lamp \equiv 1 day Florida midday, midsummer

This equation was used to re-calculate the half-lives of SWSF under Florida sunlight from those obtained under the xenon lamp (Table 5.5). The calculations showed that the photodegradation half lives expected for C_3 alkylbenzenes under Florida summer sunlight would be 4.2-12.1 days (equivalent to 11.8-33.6 hr determined under the xenon lamp). The naphthalenes would be expected to degrade to half of their initial amounts in 3.7-7.0 days under Florida summer sun light (equivalent to 10.4-19.4 hr under the xenon lamp).

The results obtained under the xenon lamp could also be converted to give a rate of degradation at other latitudes and seasons as mentioned above. This conversion is achieved using data published by Mill (1982). This publication lists values for term L_λ which is proportional to the day average radiation from sunlight, at specific wavelengths for each of four seasons. Values of L_λ are given to cover the wavelength region 299-800 nm for each of the latitudes 20, 30, 40 and 50 °N. Figure 5.11 shows the results of applying these latitude dependent summer light intensity values. It indicates that, for example, for Kuwait (29 °N) the light intensity (~ 1.58 milliEinsteins $L^{-1} d^{-1}$) is comparable to the light intensity of Florida (25-35 °N) and consequently the photodegradation half lives of SWSF compounds should be correspondingly similar given the uncertainties in the model calculation presented in the study undertaken here.

The clear implication of the kinetics data determined in this study is that photodegradation may occur at rates which makes it an effective removal mechanism of oil components (depending on latitude and cloud cover) compared with other weathering processes. For example, the rates and magnitude of evaporation, which is probably the fastest weathering process, are heavily dependent on the composition of the oil and the prevailing

Table 5.5 Estimation of the photodegradation half lives of the seawater soluble fraction compounds of Kuwait crude oil at Florida midday midsummer sunlight (Latitude 25-35 °N, Longitude 81-85 °W, 12 hr of light per day).

Compound	Half Life ($t_{1/2}$)	
	Xenon Lamp (hr)	Florida Midday, Midsummer (day) ^a
<i>sec</i> -Butylbenzene	12.3	4.4
1,4-Dimethyl-2-ethylbenzene + 1,3-Dimethyl-4-ethylbenzene	33.6	12.1
1,2-Dimethyl-4-ethylbenzene	19.3	6.9
1,2,4,5-Tetramethylbenzene + 1,2,3,5-Tetramethylbenzene	11.8	4.2
1,2,3,4-Tetramethylbenzene	32.4	11.6
Naphthalene	15.7	5.6
2-Methylnaphthalene	12.0	4.3
1-Methylnaphthalene	14.9	5.3
1+2-Ethylnaphthalene	15.9	5.7
1,3-Dimethylnaphthalene + 1,7-Dimethylnaphthalene	19.3	6.9
1,6-Dimethylnaphthalene	10.4	3.7
2,3-Dimethylnaphthalene + 1,4-Dimethylnaphthalene + 1,5-Dimethylnaphthalene	19.4	7.0
1,3,7-Trimethylnaphthalene	12.00	4.3
1,2,4-Trimethylnaphthalene	12.4	4.5

^a 2.78 hr under xenon lamp \equiv 1 day under Florida sunlight (Parker and Leahy, 1988), see also section 5.4.6.

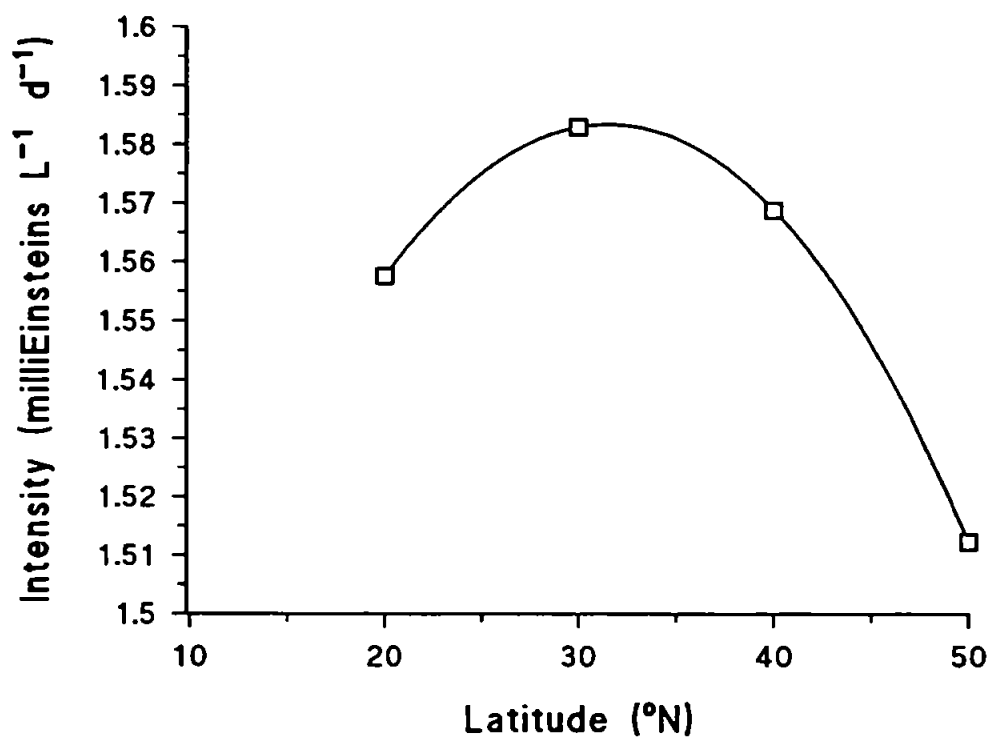


Figure 5.11 Latitude versus total summer sunlight intensities at 300-400 nm (Mill, 1982).

environmental conditions, especially wind and temperature. An estimated evaporation volume of 40-60 % for Kuwait crude oil may occur between 0-60 hr after the spill, depending on the spilled volume (the higher the volume the less evaporation). Dispersion and dissolution rates are slower and they could occur, depending on sea conditions, at 10-60% per day between 1 to 3 days and decrease to 0-10% from day 6 or more (see Doerffer, 1992).

While the above mentioned processes are most important in the short term, biodegradation and photodegradation could start after the spill and continue even after the spill has disappeared from the seawater surface. The rate of photodegradation and biodegradation in the natural environment will depend upon environmental conditions, as different limiting factors would be operating. For example, it has been argued that in tropical waters, the rate of biodegradation is limited by the rate of nutrient supply and given the intensive solar radiation and temperature of tropical regions, photodegradation may then become the major degradation process. In contrast, under conditions where light is limited, such as in arctic regions, photodegradation may be minimal and biodegradation is the main process.

Tabak *et al.* (1992) formulated a computer model for the prediction of the biodegradability of a number of organic pollutants including some alkylbenzenes. The Ln biodegradation first-order rate constant (k_{bio}) for butylbenzene (structure of butyl group not stated), for example was reported as $(-2.99) \sim (-3.27)$. The Ln photodegradation pseudo first-order rate constant (k_p) determined in the present study for *sec*-butylbenzene was -2.88. Comparing the two values and considering that different isomers degrade at different rates, suggests that photodegradation may indeed occur at a similar rate to biodegradation. The two processes are interrelated, products from photochemical process can undergo biological changes (e.g. Rontani *et al.*, 1985; 1987) and perhaps *vice versa*.

Information regarding the extent and rate of different weathering processes is useful in evaluating the persistence of crude oil in marine waters. This is important for predicting the fate of the spill and for planning an appropriate response under the circumstances. The results of laboratory studies may be useful in formulating these predictions. For example, Zepp and Schlotzhauer (1979) used computer programming to predict the direct photolysis rates and half-lives of some aromatic pollutants from data measured in the laboratory with a mercury lamp. However, as light source plays a major role in the accuracy of these predictions, the data might be better if a more appropriate artificial light source was used, such as the xenon lamp used in this study.

The photodegradation first-order rate constants and half-lives as determined in this study could be used in conjunction with data on other weathering processes, in a model which may enable the prediction of the fate of components of crude oil spills in high solar intensity regions, such as the Arabian Gulf, or lower solar intensity regions such as the Arctic and Antarctica.

5.5 Conclusions

The irradiation system established in this study proved to be reliable for the photodegradation of the seawater soluble fraction of Kuwait crude oil. The experimental setup provided constant irradiation from a representative light source at a well controlled sample temperature.

The recovery of the SWSF volatiles, such as benzene and toluene, was good with minimal variability between each of the experiments. Indeed, enhanced recovery of the deuterated internal standards, benzene- d_6 (40%), naphthalene- d_8 (79%) and phenanthrene- d_{10} (71%)

added to the SWSF sample was evident compared with the recovery of these standards alone. This confirms earlier observations about the effects of the solution concentration on the recovery of the substrate when concentrated by K-D.

C_{0,3} alkylbenzenes and some C₄ isomers showed no photodegradation under the irradiation conditions used. No apparent photosensitisation reaction seemed to have occurred. On the other hand, *sec*-butylbenzene, 1,2-dimethyl-4-ethylbenzene, 1,2,4,5- + 1,2,3,5-tetramethylbenzene and 1,2,3,4-tetramethylbenzene, showed significant first order photodegradation.

Almost all of the naphthalenes were rapidly degraded following irradiation under the experimental conditions employed here. The calculated $t_{1/2}$ of naphthalene was 15.7 hr. The $t_{1/2}$ of the 1-methyl- and 2-methylnaphthalene was 14.9 hr and 12 hr respectively. The difference in rate between 1-methyl and 2-methylnaphthalene was statistically significant and tentatively ascribed to the *peri* strain which makes the methyl group of 1-methylnaphthalene a crowded position and possibly more difficult for the abstraction of the benzylic hydrogen.

Among the C₂ alkyl naphthalenes, 1+2-ethylnaphthalene and 1,6-dimethylnaphthalene showed considerable degradation and 1,6-dimethylnaphthalene was more rapidly photodegraded than 1+2-ethylnaphthalene and the methylnaphthalenes. This was ascribed to the presence of two alkyl substitution in the 1,6-dimethylnaphthalene.

Among the C₃ alkyl naphthalenes, only 1,3,7- and 1,2,4-trimethylnaphthalene were found to be degraded and were very similar in their behaviour. The low initial concentration of some of the other C₃ alkyl naphthalene isomers resulted in a loss of accuracy in the

integration of peak areas.

The overall evaluation of the photodegradation of benzene and naphthalene compounds present in the SWSF of Kuwait crude oil showed that under the experimental conditions used, degradation occurred between 10 and 34 hr of irradiation under the xenon lamp. These results predict that the low density fraction of the seawater soluble fraction of crude oil (i.e. benzenes and naphthalenes), would be expected to degrade within approximately 12 days in the marine environment at latitude 25-35 °N, given the assumptions inherent in such calculations.

The detailed information obtained from this study about the photodegradation behaviour of a seawater extract of crude oil showed that photodegradation can play an important role in the breakdown of these compounds after oil discharges at sea.

CHAPTER SIX

CHAPTER SIX

FINAL CONCLUSIONS AND FUTURE RESEARCH

6.1 Final Conclusions

More than two decades have elapsed since the Torrey Canyon oil spill first stimulated media attention and raised considerable public awareness about the environmental consequences of oil pollution. Oil spillage accidents have occurred in many regions of the world, often with distressing results. A major oil spill may put at risk, either directly or indirectly, a wide variety of marine resources and consequently the livelihoods of many people. It is inevitable that pollution due to oil in the marine environment will remain a serious and unpredictable problem.

One of the initial stages of the weathering of oil spillage on sea involves dissolution in which the soluble fraction of oil leaches into and mixes with seawater. Since the resultant form of the oil hydrocarbons (i.e. surface oil, dispersed and emulsified, adsorbed onto particulate matters or a true water soluble fraction) influences their behaviour in subsequent degradative and uptake processes, understanding the processes that bring about dispersal of spilt oil, as well as the physical and chemical characteristics of the resulting mixture, are important prerequisites to understanding the fate and effects of petroleum hydrocarbons in marine ecosystems.

Despite considerable efforts aimed at providing information about the various weathering processes acting to remove oil spills, much work remains to be completed. The work

detailed in this thesis contributes towards a greater understanding, by providing quantitative and qualitative information about the dissolution kinetics of a crude oil (Kuwait crude oil) in seawater. Subsequent photochemical degradation of the resulting seawater soluble fraction components (SWSF) under simulated environmental conditions in the laboratory has been described.

The specific aims laid out for this study and their achievements are outlined below.

- 1. To devise an experimental procedure for the dissolution of Kuwait crude oil in seawater for use in photodegradation experiments and to monitor the dissolution by ultraviolet fluorescence spectroscopy (UVF) and dissolved organic carbon (DOC) analysis.**

Few attempts have previously been made to develop a standardised procedure for the preparation of a homogeneous and saturated solution of a seawater soluble fraction. Of the studies which have reported procedural details, many have not given sufficiently detailed descriptions to allow reproduction of the work. The series of dissolution experiments made in the course of this study demonstrated that the preparation of a homogeneous, equilibrated, seawater soluble fraction is a complex process. The factors influencing the characteristics of the dissolution were investigated. A particular problem for the preparation of reproducible WSFs involved the formation of an oil-in-water emulsion which was influenced to a large extent by the stirring rate. This problem was overcome by carefully controlling the stirring rate of seawater overlain with crude oil during preparation. By controlling the stirring rate and temperature, avoiding losses of analytes in a closed apparatus and use of a reproducible sampling technique, a dissolution procedure was formulated (Ali *et al.*, 1994). The dissolution method has the advantage of being a

simple, practical and reliable means of preparing SWSFs which should be adaptable to any light-medium crude oil.

The careful conditions under which the dissolution was carried out enabled a saturated, stable and homogeneous SWSF of fresh unrefined Kuwait crude oil to be prepared. The time required to produce the saturated solution was monitored by UVF and verified by a DOC method. The analytical conditions for UVF and DOC analysis were also optimised. In particular, the effects of heat, fluorescence quenching and loss of volatiles were investigated and consequently reproducible analyses of SWSF were achieved. As quantification by UVF depends on the match of calibrant and analyte composition, diesel oil provided the best calibrant due its similarity to SWSF. The dissolution of Kuwait crude oil using the optimised procedure increased steadily over a 10 day period. Dissolution equilibrium was achieved using an oil to water ratio of 1:100 after 5 days of slow stirring at $25 \pm 1^\circ\text{C}$. Whilst a general agreement between the two methods of analysis was demonstrated and provided an adequate means of monitoring the kinetics of oil dissolution, determination of the photodegradation kinetics required accurate measurements of the components present in the SWSF before and after photolysis. This provided a basis for the next stage of the study.

2. To optimise the method for the analysis of SWSF samples and of oil in order to determine qualitatively and quantitatively the individual compounds present.

A reliable method for the quantitative characterisation of components in SWSF was developed and optimised. Special attention was given to the efficient recovery of components and to the adoption of an appropriate analytical method. These included use

of *n*-pentane for sample extraction along with the addition of appropriate amounts of deuterated internal standards (benzene- d_6 , naphthalene- d_8 and phenanthrene- d_{10} were used) and a controlled evaporation using a micro Kuderna Danish (K-D) evaporative concentrator. The recovery experiments made using K-D and solutions of the deuterated compounds was found to range from 21-32% for benzene- d_6 to 51-102% for phenanthrene- d_{10} thus allowing even the most volatile dissolved hydrocarbons to be determined. In addition, the method was further optimised for the volume of final concentration, the storage conditions which best preserved the integrity of extracts awaiting analysis and the reproducibility of the analysis.

Examination of the equilibrated seawater fraction of a Kuwait crude oil confirmed previous studies of various crude oils prepared using slow stirring techniques. The SWSF mainly contains low-medium molecular weight aromatic hydrocarbons. The principal groups were the alkylated benzenes (C_0 - C_4) and alkylated naphthalenes (C_0 - C_3) although other minor classes of higher molecular weight were also observed. The partition coefficient between the oil and seawater ($K_{oil/sw}$) was determined by comparing the concentrations of components identified in the SWSF with their concentrations in the fresh oil. It was shown that partition of an individual hydrocarbon between the oil and seawater phases is controlled by its intrinsic hydrophobic behaviour and is similar to that in the octanol-water system. The partition coefficients calculated should allow for the quantification of the amount of hydrocarbons that may be dissolved following an oil spill at sea. These data support the contention that dissolution contributes to the continual loss of low to medium molecular weight components from crude oil discharged into water.

Detailed identification and quantification of the isomeric compounds within each group

(more than 50 compounds were characterised, Table 3.9) extended previous observations on the chemical composition of a seawater soluble fraction of crude oil (Ali *et al.*, 1993). These findings, specifically, the identification of individual isomers within the alkylbenzenes and naphthalenes, have particular relevance to toxicity studies, where the environmental implications of the identity of the dissolved chemical components are of major importance (Saethre *et al.*, 1984).

The characterised SWSF provided a suitable substrate for controlled photodegradation experiments which were achieved in the next stage of the study.

3. To develop and establish a reproducible photolysis methodology for studying photodegradation under conditions which simulate the natural environment, using a model oil aromatic compound, phenanthrene, and characterisation of the transformation products.

Simulation of solar irradiation methodology was successfully established using a calibrated high power filtered xenon lamp (194 W m^{-2}) after a series of three preliminary experiments. Furthermore, the method proved to be reproducible in a fourth photodegradation experiment. The elevation of temperature caused by heat from the xenon lamp was controlled using a high power chiller.

The photodegradation of phenanthrene under the experimental conditions used in this study was found to follow pseudo first-order kinetics. The photodegradation rate constant (k_p) at 25°C calculated from experiment 3 was $-0.342 \pm 0.003 \text{ hr}^{-1}$ ($t_{1/2}$ 2.0 hr) and $-0.317 \pm 0.03 \text{ hr}^{-1}$ ($t_{1/2}$ 2.2 hr) in experiment 4. Extrapolating these half lives to latitude 30°N

(Florida, midday, midsummer) showed that phenanthrene would photodegrade in 8.6-9.5 hr.

Interestingly, the quantitative determination of the photodegradation of phenanthrene by direct UVF analysis demonstrated a reasonable agreement with that obtained by GC-MS and allowed for direct comparison between the two methods of analysis. The photodegradation products which were detected included fluorene, fluorenone, 2,3:4,5-dibenzoxepin, 2,2'-diformylbiphenyl, 3,4-benzocoumarin and 9,10-phenanthrenequinone (Ali et al., 1993). However, the concentrations were low (11.6 % of the initial mass of phenanthrene) and the majority of the starting material was unaccounted for.

Most significantly, the established irradiation methodology proved to be reliable and was therefore used for the irradiation of the Kuwait crude oil SWSF in order to determine the photodegradation kinetics. This was achieved in the next and last stage of the study.

4. To examine solar-simulated photolysis of SWSF of Kuwait crude oil by following the photodegradation of individual components.

The photodegradation experiments resulted in good recovery of the SWSF volatiles, such as benzene and toluene, and minimal variability between each of the experiments which reflected the careful planning of these experiments. A close agreement between the results of the recovery studies conducted in Chapter 3 and in Chapter 5 was demonstrated. Such studies are essential for the assessment of the photodegradation behaviour of SWSF.

The statistical analysis of the results of each SWSF compound after irradiation, which

included the correlation coefficient, coefficient of determination, significance level, significance test and standard error of estimates, provided means for evaluating the statistical significance of the degradation kinetic rate constants (k_p). The photodegradation rate constants were considered significant at p value < 0.05 (5%).

Those benzene compounds ($C_{0,3}$ and some C_4 isomers) which possess absorption coefficients below 290 nm showed no photodegradation under the irradiation conditions used (up to 48 hr irradiation, xenon lamp $\lambda > 290$ nm, at 25 °C). No apparent photosensitisation reaction seemed to occur even though natural seawater, which should contain a variety of photosensitizers including humic substances, was used in the study. Photooxidation due to singlet oxygen 1O_2 or molecular oxygen (dioxygen) was also not apparent. This may indicate a lack of sufficient oxygen in the irradiated SWSF solution.

The photodegradation of some C_4 alkylbenzenes isomers, viz: *sec*-butylbenzene, 1,2-dimethyl-4-ethylbenzene, 1,2,4,5- + 1,2,3,4-tetramethylbenzene and 1,2,3,4-tetramethylbenzene, followed a pseudo first order rate reaction. Coelution of some of these isomers prevented the determination of $t_{1/2}$ of individual isomers. However, the differing photodegradation rates and half lives which were obtained for these isomers has environmental implications, particularly with respect to the toxicity of the breakdown products. This underlines the importance of isomer specific studies, such as that conducted here, in the assessment of hydrocarbon pollution.

Unlike the benzenes, almost all of the naphthalenes were rapidly degraded upon irradiation. This was facilitated because naphthalenes absorb light in the UV-B region of the radiation spectrum. The calculated half lives were between 10 hr for

1,6-dimethylnaphthalene and 19 hr for 1,3- + 1,7-dimethylnaphthalene. The half life of naphthalene was 15.7 hr, of 1-methyl- and 2-methylnaphthalene was 14.9 hr and 12 hr, respectively and that of 1,3,7- and 1,2,4-trimethylnaphthalene were both approximately 12 hr. However, the low initial concentration of some of the other C₃ alkyl naphthalene isomers made accurate measurement of their photodegradation kinetics difficult. Direct comparison with literature values was not possible because of the limited nature of similar studies. Nevertheless, agreement with literature findings has been demonstrated with regard to the rapid degradation of the methyl substituted naphthalenes compared to the unsubstituted parent compound naphthalene (Ehrhardt *et al.*, 1992).

The photoreactivity demonstrated by the C₄-alkylbenzenes and the naphthalene isomers indicated a link between the rate of photodegradation of the isomers and the nature of isomer substitution. This has confirmed the observations of previous workers but the reasons for this behaviour are not yet understood (e.g. Klein and Pilpel, 1974b; Sydnese *et al.*, 1985b; Fukuda *et al.*, 1988).

Extrapolation of the laboratory determined half lives of benzene and naphthalene compounds present in the SWSF of Kuwait crude oil predict that degradation of these compounds would be expected within approximately 12 days in the marine environment at latitude 25-35°N. These kinetic data may prove valuable in formulating a model for the prediction of the fate of oil released into the aquatic ecosystems.

This study has increased our understanding of some aspects of the fate of oil in the marine environment. It has provided detailed information about the dissolution/partitioning processes of crude oil components in seawater and the photodegradation behaviour of the

resulting seawater extract and showed that photodegradation can play an important role in the breakdown of these compounds after oil discharge. The calculated photodegradation rates, together with data from other weathering processes (eg. evaporation, dissolution, biodegradation) provide a means of predicting and studying the ultimate fate of oil discharged into the sea whether major acute oil spills or more continuous, chronic effluent discharges.

6.2 Recommendations for Future Work

The present study has formed the basis for further photodegradation research work. After appropriate modification the established experimental methodology for characterising (qualitatively and quantitatively) components of a seawater soluble fraction before and after photolysis may also be applicable to the study of other organic pollutants (e.g. organochlorine and organophosphate pesticides). This would enable the effect of solar radiation on the disappearance and transformation of such chemicals in the aquatic environment to be determined.

Research into the photodegradation of oil hydrocarbons under realistic environmental conditions could be modified, expanded and further studied in areas summarised below.

Analytical Methodology

- 1. To use authentic compounds, singly or in limited number, and also to use larger volumes of SWSF for photolysis to achieve more reliable quantification and further information concerning the photodegradation kinetics.**

A seawater soluble fraction was found to be a useful substrate to study the photodegradation of oil components because it provided a simplified approach to studying the abiotic degradation of oil spills. However, the low solubility and the high partition coefficient of some of the higher molecular weight components (e.g. C₃ alkyl naphthalenes, dibenzothiophenes), which are also the most photolabile species, limited the extent of oil compounds that could be investigated. Determination of the photodegradation rates of these compounds was made more difficult because of the low initial concentrations even when using a sensitive detection technique such as GC-MS.

This difficulty could be overcome by using the following approaches:

(i) The study of phenanthrene as a single model compound has proved successful in obtaining useful information on the degradation kinetics and the characterisation of the photoproducts. This approach should be similarly applied to other compounds. By studying either a single component or a small group of isomeric compounds similar in chemical structure (e.g. Sydnes *et al.*, 1985b) or a limited number of aromatic compounds differing in chemical structure (e.g. Mill *et al.*, 1981), much useful information could be gained. This approach is advantageous mainly because it would allow higher concentrations of the authentic compounds to be prepared; although the solubility limits should not be exceeded. Furthermore, it would make the identification of the transformation products easier, partly as a result of using higher starting concentrations of the studied compound(s) and partly as a result of using a less complex mixture. The information gained could then be applied to the same compounds in complex mixtures (e.g. oil).

(ii) By using a larger volume of samples for photolysis, e.g. 1 L, higher amounts of SWSF

components could be extracted and thus higher detection limits could be obtained after a longer irradiation periods. Modification of the photolysis cells and sample temperature control are required to allow for this approach and the number of samples that could be irradiated at one time would be reduced. Use of a larger volume for photolysis would be more reliable because it would increase the amount of solute and make quantification more accurate.

2. To investigate an alternative sample preparation method.

The efficient extraction, concentration and recovery of SWSF components were important to the accurate characterisation of each constituent. The methods developed in this study have proved to be useful and adequate. However, alternative methods which reduce the time and the number of steps involved in the preparation procedure, and produce minimal losses would be invaluable particularly because large numbers of samples are often required for photolysis studies. Solvent-free sample preparation techniques using solid phase micro extraction such as that proposed by Otu *et al.* (1993) may prove to be useful. The technique is still in the developmental stage but may prove to be worthwhile in the future.

3. To characterise the high molecular weight envelope of the SWSF.

A feature of the GC-MS analysis of SWSF was the presence of a complex mixture of high molecular weight and polar aromatic compounds in low concentration. Very few studies have attempted to characterise the unresolved complex mixture in the SWSF (*cf.* Burwood and Speers, 1974), but it may be possible to achieve more useful information if this

mixture could be fractionated. Simple fractionation techniques such as thin layer chromatography (TLC) or open column chromatography followed by GC-MS analysis of the isolated fractions may prove helpful. Employing special stationary phases with GC or GC-MS analysis could provide an alternative. Techniques such as high performance liquid chromatography (HPLC) which would allow fractionation according to ring number could also be investigated. These methods could assist the separation and consequently the characterisation of the photoproducts that may form upon irradiation.

Photodegradation Research

The high power xenon lamp introduced in this study is currently one of the best alternatives to natural solar radiation and there is considerable scope for further photodegradation research. The irradiation system established in the course of this study proved to be reliable and reproducible and may be applied to further studies in the following areas:

- 1. To study in detail the photoreactivity behaviour of SWSF components under different photolysis conditions.**

(i) According to the results of this study, benzene compounds, particularly C_0 - C_3 alkylbenzenes, did not exhibit any photodegradation behaviour. However, Ehrhardt and Petrick (1984) demonstrated the photodegradability of some alkylated benzenes in the presence of anthraquinone (a carbonyl photosensitiser). It would be of interest to investigate the role of photosensitisation on the photochemical reaction of this group of compounds and also on other oil hydrocarbons such as *n*-alkanes, which possess an

absorption wavelength that does not overlap with the wavelength spectrum of the light source.

(ii) It is also necessary to establish the effect of other factors such as temperature, oxygen, and light intensity on the photodegradation rate and the transformation products. The photolysis conditions can be varied and incorporated in irradiation model conditions to simulate areas with lower intensity of solar radiation, such as Britain. The kinetic information can then be compared with studies in which other factors, such as the presence of a photosensitiser or oxygen, have been incorporated.

2. To study the photodegradation susceptibilities of isomeric compounds within one group.

In view of the differing photodegradation rates and half lives observed for the degraded components (i.e. C₄-benzenes, naphthalenes) the photoreactivity of the different isomers within any one group require further investigation. This can be facilitated using the approach proposed in the analytical methodology above, in which a few isomers (which would not co-elute in the chromatographic analysis) are photolysed and studied. This approach would also allow for a better understanding of the photodegradation pathway governing the transformation of the compounds.

3. To characterise the breakdown photooxidation products and to study their toxicity.

Characterisation of the transformation products is another important area where there is

potential for further research. The susceptibilities of different compounds to photodegradation, as seen from the result of this study, have important implications with respect to the amount of toxic breakdown products and this should be investigated further. One method which could facilitate the identification of the photoproducts is using ^{14}C radiolabelled compounds which was suggested in the case of phenanthrene (Chapter 4) to follow the breakdown / transformation products and to allow for quantitative budgeting. It may be useful if the toxicity studies were made with selected biota which represent the marine environment where these photooxidation products are likely to form, such as in the Arabian Gulf or tropical areas such as Bermuda (Ehrhardt and Petrick, 1984; Ehrhardt and Burns, 1993). In addition the analysis method developed in this study has proven to be reliable for the detection and quantitative determination of photoproducts as demonstrated in the case of phenanthrene. Nevertheless, further development is needed. A standardised method would allow comparison of studies carried out in different regions of the world in view of the importance of including hydrocarbon oxidation products in environmental assessment studies (Burns, 1993).

4. To formulate a "fate of oil" prediction model.

Formulation of a predictive model using the data generated from this study (i.e. dissolution, partition coefficient, photodegradation) together with data on evaporation and biodegradation rates should be attempted. An effort should be made to construct a mathematical computer model to provide a picture of the behaviour of spills in order to provide an objective assessment of the severity of a spill in relation to physical and chemical data specific to that environment.

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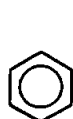
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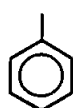
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APPENDICES

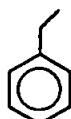
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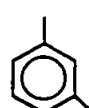
Benzene



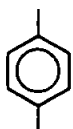
Toluene



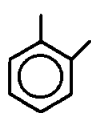
Ethylbenzene



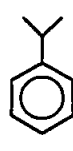
1,3-Dimethylbenzene



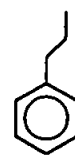
1,4-Dimethylbenzene



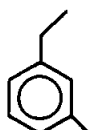
1,2-Dimethylbenzene



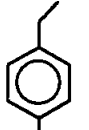
Isopropylbenzene



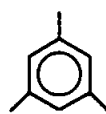
n-Propylbenzene



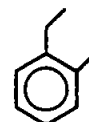
1-Ethyl-3-methylbenzene



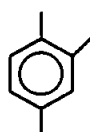
1-Ethyl-4-methylbenzene



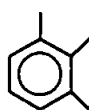
1,3,5-Trimethylbenzene



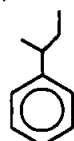
1-Ethyl-2-methylbenzene



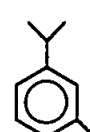
1,2,4-Trimethylbenzene



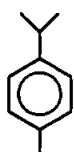
1,2,3-Trimethylbenzene



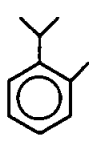
sec-Butylbenzene



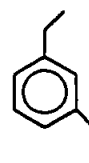
1-Isopropyl-3-methylbenzene



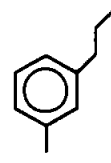
1-Isopropyl-4-methylbenzene



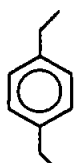
1-Isopropyl-2-methylbenzene



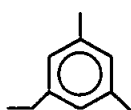
1,3-Diethylbenzene



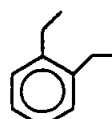
1-Methyl-3-propylbenzene



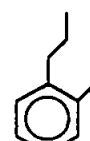
1,4-Diethylbenzene



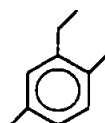
1,3-Dimethyl-5-ethylbenzene



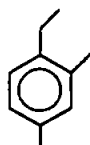
1,2-Diethylbenzene



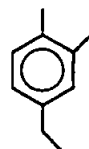
1-Methyl-2-propylbenzene



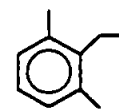
1,4-Dimethyl-2-ethylbenzene



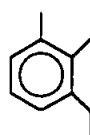
1,3-Dimethyl-4-ethylbenzene



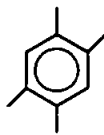
1,2-Dimethyl-4-ethylbenzene



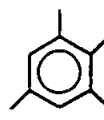
1,3-Dimethyl-2-ethylbenzene



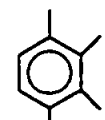
1,2-Dimethyl-3-ethylbenzene



1,2,4,5-Tetramethylbenzene



1,2,3,5-Tetramethylbenzene



1,2,3,4-Tetramethylbenzene

Structures of alkylbenzenes (C_0 - C_4) identified in the seawater soluble fraction of Kuwait crude oil.

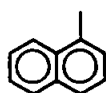
Appendix 1 "Continued"



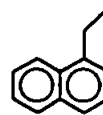
Naphthalene



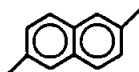
2-Methylnaphthalene



1-Methylnaphthalene



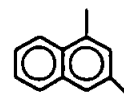
1-Ethylnaphthalene



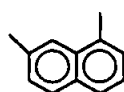
2,6-Dimethylnaphthalene



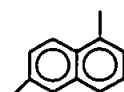
2,7-Dimethylnaphthalene



1,3-Dimethylnaphthalene



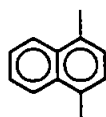
1,7-Dimethylnaphthalene



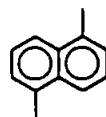
1,6-Dimethylnaphthalene



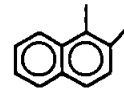
2,3-Dimethylnaphthalene



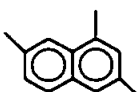
1,4-Dimethylnaphthalene



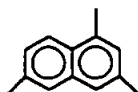
1,5-Dimethylnaphthalene



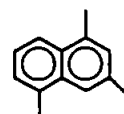
1,2-Dimethylnaphthalene



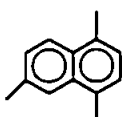
1,3,7-Trimethylnaphthalene



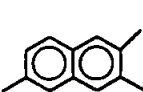
1,3,6-Trimethylnaphthalene



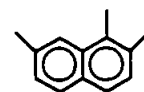
1,3,5-Trimethylnaphthalene



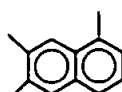
1,4,6-Trimethylnaphthalene



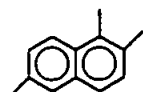
2,3,6-Trimethylnaphthalene



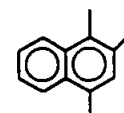
1,2,7-Trimethylnaphthalene



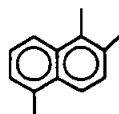
1,6,7-Trimethylnaphthalene



1,2,6-Trimethylnaphthalene

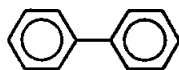


1,2,4-Trimethylnaphthalene

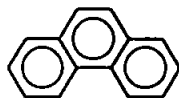


1,2,5-Trimethylnaphthalene

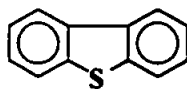
Structures of alkylnaphthalenes (C_0 - C_3) identified in the seawater soluble fraction of Kuwait crude oil.



Biphenyl



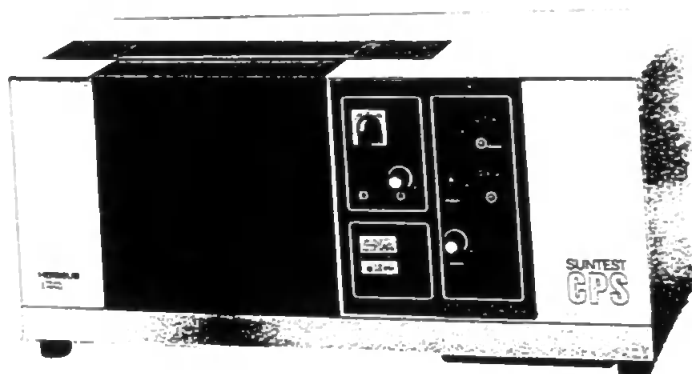
Phenanthrene



Dibenzothiophene

Structures of other compounds identified in the seawater soluble fraction of Kuwait crude oil.

Appendix 2



SUNTEST CPS - Heraeus Instruments

Low cost table top unit for quick testing in any location, with controlled and adjustable irradiance.

Irradiance:	765 W/m ²
(maximum, $\lambda < 800$ nm; without additional filters)	

Exposure area:	approx. 500 cm ² (800 square inch)
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Cooling air requirement:	120 m ³ /h
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Dimensions:

Height:	350 mm (13.8")
Width:	780 mm (30.7")
Depth:	350 mm (13.8")
Weight:	approx. 28 Kg (61.7 lb)

Voltage:	208-240 V \pm 10 %, 50/60 Hz
Rating of machine:	2,1 KVA
Rating of Xenon burner:	1,8 KW
Current consumption:	14,6 A

Appendix 3



Chiller Thermocirculator - CONAIR Churchill

Provides constant temperature controlled by re-circulation of heated or cooled liquids with adjustable temperature scale.

(Model 05/CTC HG)

Compressor nominal HP: 0.5
Cooling capacity: 700 Watt 0 °C

Temperature range: -20 to +25 °C
(below +5 °C using antifreeze)

Low standard temp. limit: +5 °C

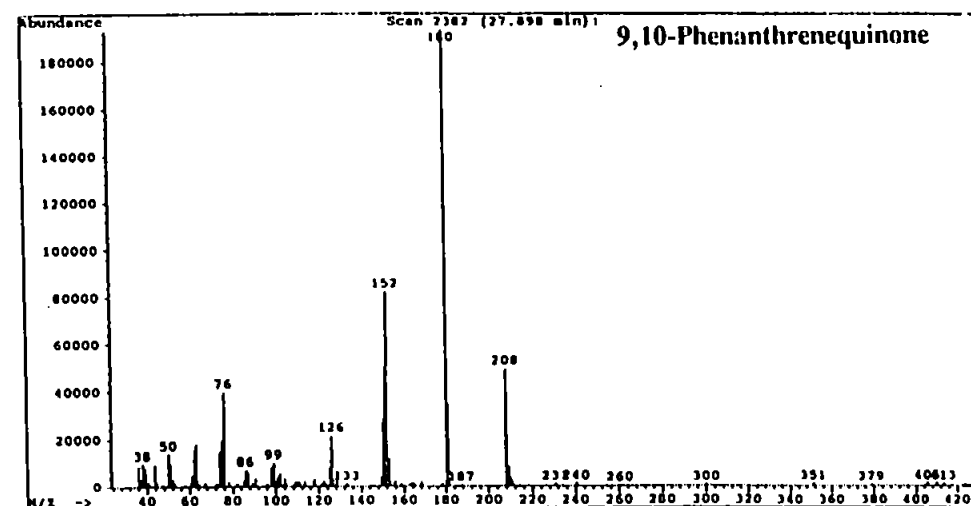
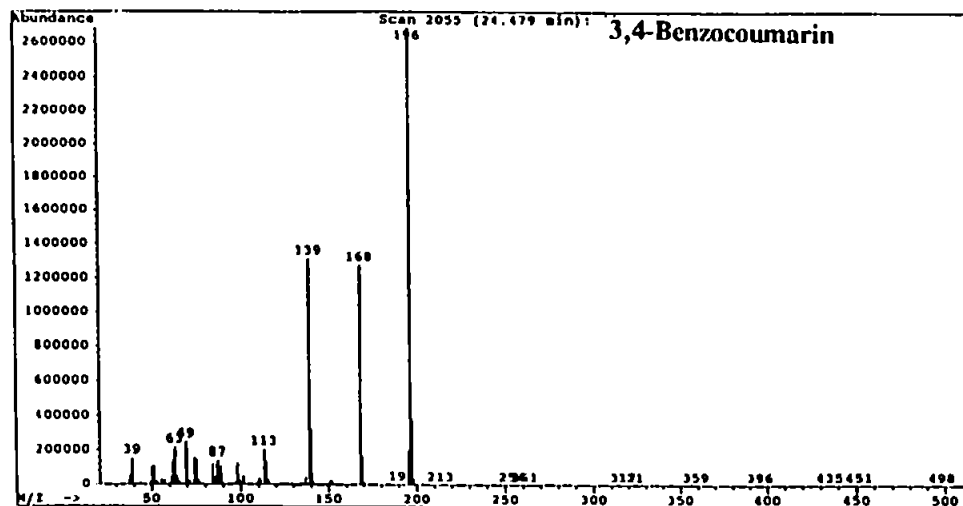
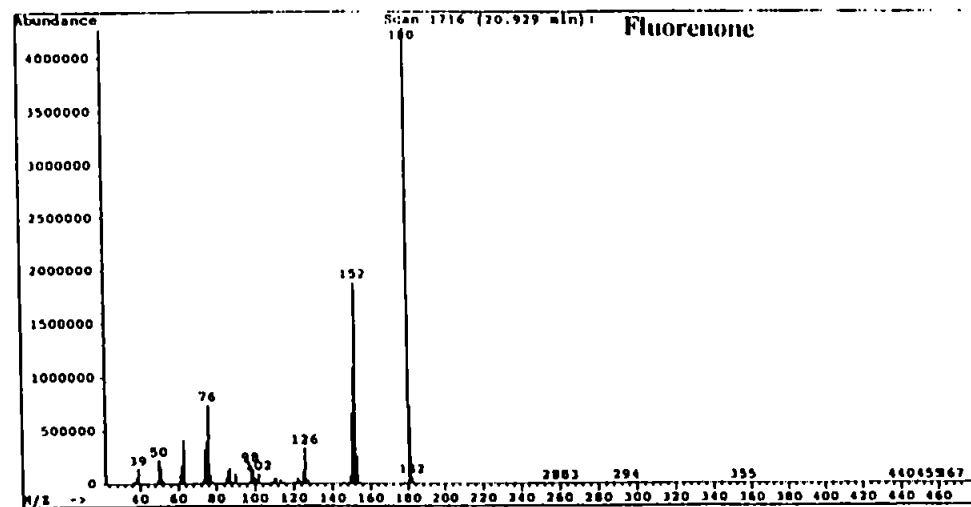
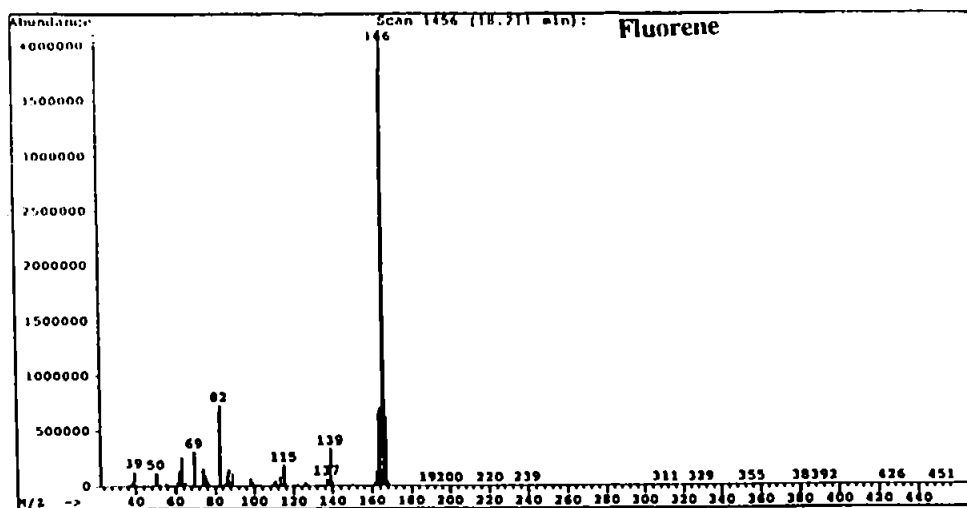
Pump - max flow: 40 L/m (8.8 g/m)
Pump - max pressure: 0/42 bar (6 psi)
Pump - type: Glandless magnetic drive

Dimensions:

Height: 464 mm (18.25")
Width: 380 mm (15")
Length: 634 mm (25")
Weight: 59 Kg

Connections: Hose tail 2 x 16 mm
Electrical supply: 220/240 V 50 Hz: 1ph 6A

Appendix 4



Mass spectra of the authentic photodegradation products of phenanthrene formed upon irradiation under xenon lamp.

Appendix 5

RESEARCH PAPERS AND POSTERS PRESENTED AT SCIENTIFIC MEETINGS

"Experimental Development Studies on the Photodegradation of the Water Soluble Fraction of Kuwait Crude Oil", Poster presented at the 16th International Meeting of Organic Geochemistry, Stavanger, Norway, 20-24 September, 1993.

"Experimental Development Studies on the Photodegradation of the Water Soluble Fraction of Kuwait Crude Oil", Paper presented at the annual meeting of the British Organic Geochemistry Society, Plymouth, UK, 20-23 July, 1993.

"Effects of Sewage Discharges on Intertidal Ecosystem in Kuwait", Paper presented at the Marine Disposal of Waste Water Seminar, Rio de Janeiro, Brazil, 25-27 August, 1986.

"The Role and Problems of Monitoring Bottom Sediment for Pollution Assessment in the Coastal Marine Environment", Paper presented at a Symposium of the Regional Organisation for the Protection of Marine Environment (ROPME), on Regional Marine Monitoring and Research Programmes, University Al-Ain, Al-Ain, United Arab Emirates, 8-11 December, 1985.

"Interaction Between Tidal Water and Intertidal Sediment", Poster presented at the 12th Biennial Meeting of IAWPRC., NERC., on Estuarine-Coastal Pollution, Plymouth, UK, 16-19 July, 1985.

OTHER MEETINGS ATTENDED

15th International Meeting on Organic Geochemistry, Manchester, UK, 16-20 September, 1991.

British Organic Geochemistry Society Meeting, Bideford, Devon, UK, 30 August -1 September, 1990.

15th IAWPRC Biennial International Conference and Exhibition on Water Pollution Research and Control, Kyoto, Japan, 30 July - 3 August, 1990.

4th Workshop on the Chemistry and Analysis of Environmental Hydrocarbons, Strasbourg, France, 19-21 April, 1990.

14th International Meeting on Organic Geochemistry, Paris, France, 18-22, September 1989.

British Organic Geochemistry Society Meeting, Liverpool, UK, July, 1989.

14th IAWPRC Biennial International Conference and Exhibition on Water Pollution Research and Control, Brighton, UK, 17-23 July, 1988.

13th IAWPRC Biennial International Conference and Exhibition on Water Pollution Research and Control, Rio de Janeiro, Brazil, 17-22 August, 1986.

PUBLICATIONS

Ali, L.N., Mantoura, R.F. and Rowland, S.J. The dissolution and photodegradation of Kuwait crude oil in seawater. 1-Quantitative dissolution and analysis of the seawater soluble fraction. *Marine Pollution Research*, (1994), In press.

Ali, L.N., Mantoura, R.F. and Rowland, S.J. Experimental development studies on the photodegradation of the water soluble fraction of Kuwait crude oil. In: *Proceedings of the 16th International Meeting on Organic Geochemistry*, Stavanger, Norway, (1993), pp. 583-586.

Literathy, P. and Ali, L.N. The role and problems of monitoring bottom sediment for pollution assessment in coastal marine environment. *Water Sciences & Technology*, (1987), 19(5/6), 781-792.

Literathy, P. and Ali, L.N. Effects of sewage discharges on intertidal ecosystems in Kuwait. *Water Sciences & Technology*, (1986), 18(11), 35-45.

Literathy, P and Ali, L.N. Interaction between tidal water and intertidal sediment. *Water Sciences & Technology*, (1986), 18(4/5), 330.