Examination of produced water from the Al-Hamada oilfield, Libya.

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Examination of Produced Water from the Al-Hamada Oilfield Libya

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Abstract

Produced water is generated to the surface from oil production. Because of the complex composition of produced water (a mixture of different organic and inorganic compounds and residues of oilfield chemicals - added to aid oil water separation) and due to the outcome of increasing volume and effect of discharging, its analysis has become a significant issue of environmental concern. For this purpose and also because of concerns over health and its safety, the chemical compositions of four produced water samples from Al- Hamada oilfield in the Libyan Arab desert were investigated in details. The -physical-chemical properties included **pH,TDS, EC, COD, cations** and **anions**, organic compounds **TOG**, **TPH, Base/Neutrals acids**, **Total phenols**, **BTEX, PAH** carbon distribution of the oil extracted from the samples ,inorganic compounds (heavy metals), added chemicals (corrosion inhibitor and biocides), Determinations were carried out using techniques, such as, **GC–FID (HS-SPME), GC–MS, (ESI-MS/MS)** and **(LC-ESI-MS).** The results indicate that the metals were within the expected natural ranges compared to those mentioned in the literature. Only manganese values were found to be higher than those in the literature in a range between **0.06-0.23**ppm .**BTEX** and phenol were within range, **0.1- 0.2**and compounds **acenaphthene , indeno(1,2,3-cd)pyrene, benzo(b)fluoranthene** of **PAH** were identified in the range between**0.4-2**ppm. These originate could be from biodegradation by existing bacteria, which generally changes the chemical composition and reduce the toxicity of the water. Typical corrosion inhibitor chemicals quaternary ammonium compounds **(quats)** were detected with alkyl chain lengths of **C12 (*m/z* 304), C14 (*m/z* 332), C16 (*m/z* 360) and C18 (*m/z* 388).** On the whole, knowledge is needed about the level of oilfield chemicals in the produced water and groundwater and also phenol and alkyl phenols compound present that contribute to the environmental impact of produced water need to identify by **GC–MS**. Produced water should not be consumed by humans and animals.

Declaration

I declare that the thesis hereby submitted for the Degree of MPhil, at Sheffield Hallam University represents my own work and has not been previously submitted by me at another University for any degree.

Huda Mohamed Harati

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Dedication

Special dedication and in memory of my father who passed away during my master studies, because he is my main moral support and to my mother who is a role model in my life, and to my dear husband who formed an important pillar of my life. I really thank them for their words of encouragement and support till the last minute of my thesis.

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AAS	Atomic Absorption Spectroscopy
bbl	Barrel (= 159 Litres)
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
CV-AAS	Cold Vapour Atom Absorption Spectroscopy
DRC-ICP-MS	Dynamic Reaction Cell Inductively Coupled PlasmA MASS Spectroscopy
ESI-MS^N	Electrospray Ionisation Multi-Stage Mass Spectrometry
EC	Electrical Conductivity
ESI-MS/MS	Electrospray Ionization Tandem Mass SpectrometrY
EPA	Environmental Protection Agency
GC	Gas Chromatography
GC-MS	Gas Chromatography Mass Spectrometry
GC–FID	Gas Chromatography-Flame Ionization Detection
GC–MS	Gas Chromatography–Mass Spectrometry
GOM	Gulf of Mexico
HS-SPME	Headspace Solid-Phase Microextraction
HPLC	High Performance Liquid Chromatography

HR-ICP-MS	High Resolution Inductively Coupled Plasma Mass Spectroscopy
HG-AAS	Hydride Generation Atomic Absorption Spectroscopy
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma- Optical Emission Spectrometry
NPD	Naphthalene, phenanthrene and dibenzothiophene
NOC	National Oil Corporation
NPDES	National Pollutant Discharge Elimination System
NORM	Naturally Occurring Radioactive Material Or
OCS	Oilfield Chemicals
PAH	Polycyclic Aromatic Hydrocarbon
Quats	Quaternary Ammonium Compounds
RO	Reverse Osmosis Membrane Separation
SAR	Sodium Adsorption Ratio
SPME	Solid-Phase Microextraction
SRB	Sulfate Reducing Bacteria.
SS	Suspended Solids

TOC	Total Organic Carbon
TDS	Total Dissolved Solids
TH	Total HydrocarbonS
TOG	Total Oil And Grease
TPH	Total Petroleum Hydrocarbon
U.S.	United States
UIC	Underground Injection Control

Chapter 1

Introduction

1. Produced water

1.1 Definition of produced water

Oil and gas extracted from oilfields in many areas of the world are accompanied by (mainly salty) water called produced water. Produced water is defined by the U.S.-EPA as the water (brine) brought up from the hydrocarbon bearing formation strata during the extraction of oil and gas. It can include formation water which is a natural water layer that, being denser, lies under the hydrocarbons, injection water, small volumes of condensed water , and residues of treatment chemicals that have been added to assist in the separation of oil/water (Produced Water Facts), to avert unfavorable effects. These can include solvents or chemicals such as hydrate inhibitors, dehydrators, scale inhibitors, corrosion inhibitors, bactericides, emulsion breakers, coagulants, flocculants, deformers and paraffin inhibitors (Farajzadeh 2004). Moreover the properties of the formation water are almost the same as produced water from oil or ordinary gas production, but its composition may be quite different (Veil *et al.* 2004), as the formation water usually has higher salt concentration, with the cationic composition generally resembling sea water, also it is more acidic.

In order to transfer and utilize the product, Produced water must be removed from the petroleum product as fully as possible (Rabalais *et al.* 1991).

At the surface the output of an oilfield is separated into an oil stream, a gas stream and a water stream (Kevin and Juniel 2003). This is normally done by pressurization and gravity separation (Rabalais *et al.* 1991).

After separation a portion of the produced water is returned to the well for oil ameliorates production (Tomasz *et al.* 2005; Israilides *et al.* 1997; Ayres and Westcot 1976), and the rest is reused or disposed of (Hongzhu and Wang 2006).The portion for disposal must be treated and its toxicity assessed

(Produced Water Facts), because it will change the reservoir composition and damage the environment. Commonly the choice for reuse relies on the quality of the produced water following treatment (Hongzhu and Wang 2006). Discharge of the produced water to deep wells for final disposal is sometimes not a suitable solution for all sites as produced water approach up to the ground level after injection into shallow wells this is discussed by (Cakmakce *et al.* 2008).

1.2 Composition of produced water

The composition of produced water is changeable between wells and within the same field (Cakmakce *et al.* 2008). It is reliant on the water, and whether it comes from crude oil or natural gas (Veil *et al.* 2004), although produced water is usually deoxygenated (Boitsov *et al.* 2007). It contains organic and inorganic substances which include largely salts and oil hydrocarbons that can contribute to the toxicity in the environment after disposal (Cakmakce *et al.* 2008). For example the concentrations of total dissolved solids (TDS) in high mineral containing components, ranges from 500-600 upwards to higher than 100,000 mg/l for coal bed natural gas (Hayes and Arthur 2004), also oil by virtue of its nature can be dispersed in water (Morrow *et al.* 1995).

The oil content can be expressed as follows:

1- Dissolved oil (aromatics containing BTEX and PAHs, acids containing fatty acids and naphthenic acids, Phenols).

2-Dispersed oil (aromatics containing mainly PAHs, acids containing fatty acids and, aliphatic) (Røe utvik 1999). However in both onshore and offshore operations, attention is concentrated on the constituents of oil and grease in produced water, and for onshore operations there are concerns over salt content (expressed as, salinity, conductivity, or TDS) as a principal constituent, inorganic and organic compounds or chemical additives used in drilling naturally accruing radioactive material (NORM) (Veil *et al.* 2004).

In general most of produced water will be contaminated by some subset or mixture of:

- Water
- Dissolved oil
- Dissolved solids
- Dissolved gases (particularly hydrogen sulfide and carbon dioxide)
- Dispersed oil droplets,
- Dispersed solid particles.
- Bacteriological matter
- Added materials (treatment chemicals, destroy fluids, acids, such as corrosion inhibitors, biocides, disinfectants, scale inhibitors, neutralizing agents (alkalinity control). (Kevin and Juniel 2003).

1.3 Techniques used for characterisation of produced water

There are a wide variety of analytical techniques used to determine the concentration of contaminants in produced water. from simple e.g. gravimetric, and titrimetric methods to very advanced techniques using specialized instrumentation such as, spectroscopy, chromatographic techniques like gas chromatography (GC), gas chromatography mass spectrometry (GC-MS) and high performance liquid chromatography (HPLC) along with spectroscopic techniques such as atomic absorption spectrometry (AAS) , inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS).Table **1.1** lists the techniques commonly used for analysing produced water.

Table1.1 Analytical techniques used to characterize produced water.

Compound	**Technique**	**Reference**
Total Oil	IR	(Tibbetts *et al.* 1992; Carey *et al.*1992)
BTEX	Purge&trap,GLCMS GC-FID	(Tibbetts *et al.* 1992) (Brendehaug *et al.* 1992; Rabalais *et al.* 1991)
PAH	GC-MS	(Tibbetts *et al.*1992; Roe *et al.* 1996; Rabalais *et al.*1991;Brown *et al.* 1992;Neff *et al.* 1992;Carey *et al.* 1992)
Organic acids	Direct GLC/FID Isotachophoresis	(Tibbetts *et al.* 1992) (Brendehaug *et al.* 1992)
Phenols	Silylation GLC-MS GC-MS Derivatisation/GC	(Tibbetts *et al.* 1992) (Grahl-Nielsen1987; Brendehaugetal.1992; Carey *et al.* 1992) (Brown *et al.* 1992)
Metals	AAS ICP-AES 3 ICP-MS 6	(Tibbetts *et al.* 1992; Neff *et al.* 1992)

1.4 Volumes of produced water

The volume of the produced water from oil and gas wells varies as the well ages (Li *et al.* 2006). The water-to-oil ratio increases over the life of a conventional oil or gas well, and this also varies from reservoir to reservoir (Li *et al.* 2006; Cakmakce *et al.* 2008). When the well is new, water makes up a small percentage of produced fluids but in time the percentage of water increases and in contrast the percentage of product declines (Li *et al.* 2006).In many instances, this waste stream is seven to eight times greater by volume than oil produced at any given oilfield.

In the U.S. water can comprise as much as 98% of the material brought to the surface, for crude oil wells nearing the end of their lives (Veil *et al.* 2004). U.S. wells generate an average of more than 7 bbl of water for each barrel of oil (Lee *et al.* 2002), while the rest of the world generate an average of 3 bbl of water for each barrel of oil (Khatib and Verbeek 2003).

Production of oil and gas in the U.S currently produces, 14-18 billion barrels of produced water every year. For instance, an EPA study indicated that 11.7 billion barrels of produced water are generated in the U.S. annually (U.S. Environmental Protection Agency 1987).

An average of 210 million bbl of water was produced each day worldwide in 1999(Khatib and Verbeek 2003).The separation, handling, and disposal of produced water lead to an estimated $18 billion costs to the oil and gas industry in the U.S. It is single largest waste stream challenge facing the oil and gas production industry (Godshall 2006). Because of the whole volume and high handling cost of the produced water, the key issue is management (Veil *et al.* 2004).

1.4.1 Factors affecting the volume of produced water during the life cycle of a well.

A number of factors can affect the volume of produced water (Veil *et al.* 2004):

- Type of well drilled
- Location of well within reservoir structure
- Type of completion
- Type of water separation and treatment facilities

- Water flooding for enhanced oil recovery
- Insufficient produced water volume for water flooding
- Loss of mechanical integrity
- Subsurface communication problems

1.5 Produced water discharging

1.5.1 Environment impacts and volumes of produced water discharged.

1.5.1.1 Environmental impact of Produced Water Discharge

In order to assess possible effect of produced water on the environment produced water must be tested for toxicity. From these data maximum discharge rates are set. Under Oil Pollution Prevention and Control OPPC 2005 installations are given a permit for activities discharging oil to sea. From 1 January 2006 the oil in produced water must not exceed 30 milligrams per litre as a monthly flow weighted average (Department of energy and climate change).

The effect on the environment depends on the site of discharging. Disposing in the open ocean has little impact or no measurable effects on marine organisms because of the dilution that takes place after discharging; on the other hand a large impact will be caused to the environment if the produced water is discharged to small streams (Veil *et al.* 2004).

Experiences to date in the USA and in other parts of the world show that there are minimal risks associated with the discharge of appropriately treated produced water (Offshore Produced Water Waste Management 2001).

The actual impact of produced water discharge on living organism can achieve is determined by several variables like the physical and chemical properties of the constituents, temperature, the content of dissolved organic material, humic acids, presence of other organic contaminants, and internal factors such as metabolism, fat content, reproductive state, and feeding behaviour (Frost *et al.* 1998) .

As a rule the physical/chemical character of produced water (little dissolved oxygen and pH, elevated salinity and metals) does not pose a hazard (Wills 2000), but magnesium, calcium, sodium and chloride are major contributors to salinity in water and may have high TDS levels, which can have toxic effects for human or livestock consumption (Rawn- Schatzinger *et al.* 2003).

Aromatic and phenol fractions of the dissolved hydrocarbons are the main contributors to the acute toxicity (short - term effects) of produced water that may cause localized impact (Frost *et al.* 1998).

The toxicity of the soluble organic fraction of produced water is not known (Veil *et al.* 2004).

The toxic effects of produced water on living organisms may be due to absorption of water-soluble components through the surface epithelia (e.g. body surface and gills) and/or to oral ingestion and digestion of particulate material. In fact a number of studies have pointed out that the acute toxicity of produced water to marine organisms is generally low, excluding possibly in the mixing zone, due to the rapid dilution and biodegradation of the aromatic and phenol fractions (Frost *et al.* 1998; Brendehaug 1992).

Refractory organic pollutants are highly toxic and not simply degraded in the environment. Chronic toxicity testing is required for offshore oil and gas operations according to the EPA permit. Results of this testing In U.S Waters do not indicate any significant toxicity problem. Some of the North Sea nations have focused their attention more heavily on the combined impact of many chemical constituents and the produced water controlled by different approach (Veil *et al.* 2004).

1.5.1.2 Volumes discharged

Produced-water re-injection percentage rises to greater than 90% when produced water from oil and gas operations is considered together (Produced Water Facts).

The amount of produced water discharged from Norwegian oil and gas production which is about 30% of the produced water discharged to the entire North Sea, in 1992 was close to 23 million m^3, 26 million m^3 in1993 (Strømgren *et al.* 1995), roughly 100 million m^3 was discharged in 2000 and in 2003 the volume was close to 400 million m^3, This means that produced water volumes have tripled since 2000 (Wright *et al.* 1994*).* This water contains tens of thousands of tonnes of organic compounds, including hundreds of tonnes of alkyl phenols (Olf 2006). Alkyl phenols are known as prospective endocrine disruptors which makes them a matter of concern for marine biota (Nimrod and Benson, 1996; Meier *et al.* 2007), Heavy oil-produced water annually discharged into the environment from the Liaohe Oilfield in China is about 20 million m^3. The National Research Council (1985) estimates that worldwide produced water estimates to the oceans is less than 0.4% of the total amount of petroleum hydrocarbons (Offshore Produced Water Waste Management, 2001). On the other hand 65% of the produced water generated in the U.S. is injected back into the producing formation, 30% into deep saline formations and 5% is discharged into surface waters (Cakmakce *et al.* 2008). The average annual volume of produced water in Ecuador was equivalent to 1.7 times the total volume of water disposed onshore in the U.S. in 1985. (American Petroleum Institute (API) 1987). Table **(1.2)** indicates discharged volumes in the North Sea and produced water production discharge from Canadian East Coast fields to date shows in Table**1.3**; however discharge patterns from this field to date have been consistent for fields in other areas of the world.

Table 1.2 Produced water discharged in the North Sea (1996-1998) (Wills *et al.* 2000).

Year	Number of installations	Water quantity (millions of tonnes)	Oil levels (ppm)	Oil quantity (tonnes)
1996	59	210	27	5,706
1997	64	234	25	5,764
1998	67	253	22	5,690

Table 1.3 Produced water production discharged from Canadian East Coast Fields (Offshore Produced Water Waste Management 2001).

Field	Cumulative Production(10^6m^3)			Platform type	PW Treatment	Status
	Oil	**Gas**	**Water**			
Hibernia	15.4	3.889	58.5	Gravity	Hydro cyclone	Active
Sable	N/A	2.059	13	Steel	Hydro cyclone	Active
Island Cohasset	7.1	N/A	14.371	Steel	Hydro cyclone	Shut in

1.5.2 Discharging limited rate of produced water

Although produced water is treated it still has traces of oil, so it is important that all new platforms are equipped with the best practicable means for separating oil from discharged water, Due to its quick mixing with seawater, it is most commonly discharged into the sea (Wills *et al.*2000). Discharge into the sea is firmly controlled by legislation, and environmental rules are becoming more severe over time (Frankiewicz et al. 1998)

Produced water is in fact disposed of in many ways, the common ones are :(Farajzadeh 2004**)** .

- Deep aquifer injection
- Surface discharge/overboard disposal
- Shallow water aquifer recharge
- Industrial use (Dust control, Vehicle wash water, power generation…)
- Agricultural use (Irrigation of fruit trees or forage land…)
- Produced Water Re-Injection (PWRI)
- Evaporation pits
- Desert flooding / livestock water pits

In the U.S. injection is regulated under the Underground Injection Control (UIC) program which is authorized by the EPA, and then controls the injection activities to guarantee protection of underground sources of drinking water (Veil *et al.* 2004).

The water quality for overboard disposal must be higher than that used for re-injection (Frankiewicz *et al.* 1998).

In the U.S most offshore produced water is discharged under the authority of general permits issued by EPA regional offices. These permits are part of the National Pollutant Discharge Elimination System (NPDES) program (Veil *et al.* 2004)

According to the total amount of waste water allowed to be discharged from each platform, each national authority should set limits these limits include limits on oil and grease that should be less than 29 mg/l as determined by the gravimetric analytical method U.S. EPA 1664, toxicity, and other constituents. This limit should be set for each platform individually for example, in the North Sea; the limit is in the practice of being decreased from 40 mg/l to 30 mg/l as determined by solvent extraction and an IR measurement. While in the two very large growth areas for oil production (including much of South America, and West Africa), the TOG discharge limits are <20 mg/l. However TOG measurements reported often do not specify the measurement method (Frankiewicz *et al.*1998). Anything above 100ppm must be reported as an oil spill (Wills *et al.* 2000).

1.5.3 Some problems associated with produced water:

- Plugging of discarding wells by solid particles and suspended oil droplets
- Plugging of lines, valves, and orifices due to deposition of inorganic scales.
- Corrosion caused by acid gases and electrochemical reactions of the water with piping and vessel walls.
- Exceeding permitted discharged oil concentrations.
- Growth of bacteria that plug lines and valves or result in the formation of detrimental products (Produced Water Facts).

1.6 Produced water management and treatment

1.6.1 Produced water management

Options for reclaiming produced water for beneficial use and/or disposal are required. There are several options for managing produced water some of them are as follows:

1.6.1.1 Minimising the amount of produced water that reaches the surface

This includes techniques that allow oil to enter the well bore while blocking water flow (like mechanical blocking devices or water shut-off chemicals) and devices that collect and separate produced water either down a hole or at the sea floor (e.g. downhole oil/water separators dual-completion wells, and sub sea separators) (Veil *et al.* 1999).

1.6.1.2 Recycling and reuse of produce water.

The options of reuse and recycling includes underground injection to encourage additional oil production, agricultural beneficial uses for irrigation, livestock or wildlife watering and habitat, and various industrial uses (e.g. dust control, vehicle washing, power plant make-up, fire control and also aquifer recharge (Veil *et al.* 2004).

1.6.1.3 Disposal of produced water.

This option is usually used, when the previous two options cannot be used. It includes evaporation by portable misting towers. Artificially constructed wetlands can be used to treat produced water (Myers 2000), along with land application, surface discharge through the National Pollution Discharge Elimination System (NPDES) permit program. All of these options require compliance with water quality criteria. In many cases the poor performance of these options requires water quality enhancement. The factors that lead to poor produced water quality indicated by Frankiewicz *et al.* (1998) are:

- Presence of inorganic or organic solids,
- Excessive or highly varying fluid flow rates,
- Gas breakout or slugging in or into process equipment, and
- Improper chemical treatment programs.

In order to comply with water quality directives expensive economic information is required for produced water management.

1.6.2 Produced water treatment

1.6.2.1 Basis of technologies verified to treat produced water

Before produced water can be treated, it must be pretreated and several pre-treatment methods were reported by (Lee *et al.* 2002). For instance at Sandia National Laboratories and the Petroleum Recovery Research Centre at New Mexico Tech many pre-treatment methods are used, such as, chemical treatment (e.g. flocculation, disinfection and filtration) (Veil *et al.* 2004), biological treatment, polymeric absorbents, and macro-porous polymer extraction (Lee *et al.* 2002).

In addition treatment of produced water includes heat treatment, gravity separation, aeration and settling ponds also physical methods(Rabalais *et al.* 1991), such as pressure –driven processes , microfiltration(MF), ultrafiltration (UF), nano-filtration (NF) and reverse osmosis membrane separation (RO) (Vieira *et al.* 2001). Technologies which use the reverse osmosis (RO) process to treat produced water can be divided into two fundamental groups, first pre-treatment and then second, the use of reverse osmosis (Hayes and Arthur 2004). Furthermore reverse osmosis and forced evaporation are the methods of desalination of produced water. However, desalination by strained evaporation is the most costly treatment process it is used only on waters with extremely high TDS concentrations and is also supposed to be the treatment plan for the brines generated during RO treatment (Hackney and Wiesner 1996). Since the 1950s water has been purified by using constructed wetlands (CW) (Jos *et al.* 1999).These are constructed to manage process wastewater and storm water at a range of installations, with refineries, oil and gas wells, and pumping stations all using CWs (Harris *et al.* 1999; Knight *et al.* 1999). Constructed wetlands have been used in the treatment of produced water, and this is reported to be a significant method for the improvement of water quality Jackson and Myers (2003) in a study at the Rocky Mountain Oilfield Testing Centre. They discovered that wetland functions were similar to those discovered in natural wetlands (Veil *et al.* 2004).

1.6.2.1.1 Types of filtration devices

Tyrie (1998) indicated that there are several types of filtration devices used for produced water treatment, for instance some operators utilize media filters that are backwashed periodically such as filters filled with crushed walnut shells (Kozar 2000). Another type of media filter explained by Brock *et al.* (2003) that features radial flow design to let on-line cleaning of the media without having to stop for backwashing. Nicolaisen and Lien (2003) give a summary of membrane filter applications and suggested that the membranes size range is are suitable for offshore produced water in the ultrafiltration, while membranes in nano-filtration and reverse osmosis can be deployed downstream of the ultra filtration filters, if needed because of having smaller pore size. In addition Jahnsen and Vik (2003) report on a North Sea compact flotation unit that combines separation, gas flotation, and centrifugal separation in the same device (Veil *et al.* 2004).

1.6.2.2 Contaminants removed from produced water

The most attention in offshore produced water treatment technology is focused on removing oil and grease (Veil *et al.* 2004), but also treatment is required to focus on reducing TDS, concentrations of benzene, brine volumes and biochemical oxygen demand BOD which rise from soluble organics. It is also a requirement to manage suspended solids, total and fecal coli forms in the final effluent stream, to eliminate special constituents of concern, such as boron, that restrict an end use (such as irrigation). Furthermore to avoid clayey soil damage the sodium absorption ratio (SAR) must be adjusted to less than 6 (Javier *et al.* 2008)

Frankiewicz *et al.* (1998) reported that the treatment equipment selected depends on the size of the particles that need to be removed .

Equipment, such as, electrostatic precipitators, plate separators, gas flotation units, centrifuges, hydrocyclones, filter membranes and skim piles are used to get as much oil as possible out of the water, but the main part of the process is still gravity treatment (American Petroleum Institute (API) 1987). The cleanliness of water to be injected relies on the character of the reservoir that will receive the water, for example reservoirs that are fractured and of carbonate do not need water quality; 2 – 5 micron range removal of solids may be required for sandstone or other low permeability formations (Frankiewicz *et al.* 1998).

Small amount of hydrocarbons and other organic chemical, dissolved salt and metals are found in the treated produced water disposal to the ocean in U.S. (Neff 2002).

1.6.2.2.1 Oil

Residual amounts of oil can contribute to plugging of formations receiving the injection and besides represent lost profit for producers (Veil *et al.* 2004). A series of treatment chemicals is added to break emulsions or make dissolved oil more open to to oil removal treatment. The "Apre-coalescer" device proposed by Tulloch (2003) consists of a bundle of oleophilic fibres positioned inside of a flow line as the fibres provided to aggregate small oil droplets for easier downstream elimination. As this technology joining or coalescing small oil droplets into larger ones that are more amenable to removal. It was considered that the dissolved oil components may go beyond the dispersed phase. An alternative technology to deal with this problem is solvent sublation which is an adsorptive bubble separation (Valsaraj *et al.*1991a; Valsaraj *et al.* 1991b; Valsaraj *et al.* 1991c; Valsaraj *et al.* 1992). This method depends on physical processes coupled with the interactions of contaminants with small bubbles rising through the liquid column to effect the separation (Thoma *et al.*1999).

1.6.2.2.2 TDS

One of the major objectives to removal of total dissolved solids (TDS) from the produced water and for the reduction of brines requiring final disposal is that it involves some degree of demineralization. In order to make the water suitable for higher use (Hayes and Arthur 2004), Reverse osmosis can be used to remove high TDS from produced water (Sirivedhin 2004).

1.6.2.2.3 Organic compounds

Organic compounds are removed to meet biochemical oxygen demand requirements for surface discharge (pursuant to compliance with NPDES compound permits) since the BOD arises from soluble organics (Hayes and Arthur 2004). Several techniques are used for the removal of organic compounds from produced water, such as, electrofocculation, adsorption bioreactors, wetlands, ultrafilltration, nano-filtration and reverse osmosis

(Sirivedhin 2004). Furthermore, dissolved organics from offshore produced water can be removed by using fluid extraction, such as, Macro Porous Polymer Extraction (MPPE), it uses polymer particles with a low-pressure steam (Meijer and Kuijvenhoven, 2002). Volatile organic compounds can be reliably removed by packed tower aeration (PTA) or air stripping (Hackney and Wiesner 1996), while soluble volatile acids are controlled by the fouling of membrane-based desalinization processes at elevated levels (Hayes and Arthur 2004).

1.6.2.2.4 Suspended solids

A general rule of thumb for solids control is that all particulate matter bigger than one-third the average pore-throat size of the receiving formation should be removed (Reynolds and Kiker 2003).

Solids are usually treated by gravity settling or filtration such as walnut shell filtration, fiber ball media filtration, gravity-type cross flow pack separation, ceramic cross flow microfiltration and ultra-filtration (Cakmakce *et al.* 2008). For example, in some streams in coal bed natural gas (CBNG areas) suspended solids do not need treatment to achieve water quality objectives (Hayes and Arthur 2004). Suspended solids removed with enhanced filtration process, after that the performance and competence of the RO equipment maximize by treating chemicals finally the total dissolved solids with reverse osmosis (Hayes and Arthur 2004).

1.6.2.2.5 Treatment chemicals

A large variety of chemical types are used in the treatment of produced water. This can make analysis difficult (Tibbetts *et al.* 1992).

1.6.2.3 Illustration of techniques exploit in treatment of produced water

Cakmakce *et al.* (2008) studied desalination of produced water from oil production fields in Traky by membrane processes. They tested the pre-treatment alternatives of reverse osmosis and non-filtration membranes high permeate flux. Best effluent water quality is determined in different combinations to get best pre-treatment combination. They found that primary sedimentation + oil/water separator + DAF system + 1 µm ceramic or metallic cartridge filter + 0.2 µm ceramic or metallic filters gave the best pre-treatment option by means of permeate flux and water quality before RO membrane. Additionally Grini, *et al.* (2002) studied produced water to choose the best treatment technologies based on environmental impact. They described four new treatment technologies which are suitable for different produced water compositions the four technologies are :

- PECT-F (Performance enhancing coalescence technology) for enhanced removal of dispersed oil.
- MPPE (Macro porous polymer extraction) technology for removal of volatile aromatics.
- C Tour technology for the removal of heavy aromatics and alkylated phenols.
- Farmhouse C100 injection system for H_2S scavenger.

Environmental Impact Factor (EIF) is calculated before and after applying the technology to show the reduced environmental impact obtained. Knowledge is needed about which compounds contribute to the environmental impact of produced water before deciding which technology can be used. Technologies must then be selected according to their range of application.

Su et al. (2007) used the biological aerated filter (BAF) to treat oil-field produced water. Their results show that 76.3 % to 80.3 % of oil, 31.69 to1-57.9 % of COD, 86.3 % to 96.3 % of BOD and 76.4 % to 82.7% of suspended solids were removed efficiently.

Dissolved salts and other contaminants are found throughout the world from industrial waste waters and undrinkable brackish waters. These can be 100% removed practically by the AltelaRain™ System but this typically needs more physical space to treat a given volume of water than comparable reverse osmosis systems. Total dissolved solids were reduced from 41,700 mg/l to 106 mg/l. Chloride was reduced from 25,300 mg/l to 59 mg/l. Similarly, benzene levels were reduced from 450 ug/l to non-detectable by AltelaRain™ technology (GODSHALL 2006).

Ji *et al.* (2007), studied surface flow constructed wetland for heavy oil -produced water from China' Liaohe Oilfield treatment for three years. The results demonstrated that SFCW could remove large amounts of COD contained in produced water even though the effluent quality of the system could be operated for a long time and stayed constant. Also the results show that reed could be a feasible wetland plant for treating heavy oil-produced water .

Hongzhu and Wang (2006) confirmed that the catalytic electrochemical system is an effective method to treat oil field produced water, as both chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were reduced by over 90% in 6 min, suspended solids (SS) by 99%, Ca^{2+} content by 22%, corrosion rate by 98% and bacteria (sulfate reducing bacteria (SRB), saprophytic bacteria (TGB) and iron bacteria) by 99% in 3 min under 15 V/120.

1.7 Literature review

1.7.1 Previous studies on the composition of produced water:

1.7.1.1 Oil in produced water

A number of studies have been carried out on the chemical characterisation of produced water from fields in the North Sea (Tibbetts *et al.* 1992; Brendehaug *et al.* 1992 ; Roe *et al.* 1996), the Gulf of Mexico (Rabalais *et al.* 1991;Brown *et al.* 1992; Neff *et al.* 1992), and the coast of Canada (Carey et al. 1992).These studies concentrate on determining hydrocarbons in water including oil. In fact oil in produced water can be found in two phases dispersed or dissolved (Stephenson 1992).

Hongzhu and Wang (2006) give a summary of the current practice for the analysis and monitoring of oil in produced water in the North Sea. Different approaches have been espoused by different countries, and reference methods based on solvent extraction followed by an infrared (IR) quantification show that using a mixture of detected scattered and transmitted radiation is practical for the determination of salinity and type of salt in water. They recommended that the measurement geometry and algorithms for data analysis are indispensable. Røe Utvik (1999) examined chemicals contained in produced water from four offshore oil production platforms in the North Sea (Oseberg Feltsenter, Oseberg C, Brage and Troll B). They determined PAH and phenols by gas chromatography-mass spectrometry, organic acids by isotachophoresis, metals by atomic absorption spectrometry and also radioactivity by high resolution gamma spectroscopy. These data were compared with database values from other fields in the Norwegian sector of the North Sea, and it was noted that the concentrations of the NPDs CI-C3 alkyl homologues, and alkylated phenols declined with an increase in alkylation of the components for all fields. Also there is no correlation with the content of THC, which is used as emission standard for environmental regulation. They recommended that individual detailed chemical characterization of produced water from each platform is essential to predict the fate and effects of the discharges of produced water to the marine environment.

An approved method EPA 413.1 under the National Pollution Discharge Elimination System (NPDES) was used to determine residue weight of oil and grease gravimetrically. This method gives good results as 80% of oil and grease residue weight can be detected to water soluble, polar components in the Freon extract (Brown *et al.* 1988).

The Oil Industry applied Standard method 5520 °F which describes how to separate non hydrocarbons from hydrocarbons using (GC/MS). For example, it removes the major water soluble polar compounds from the Freon extract to about 79 to 98 % (Brown *et al.* 1992) which the major component was carbon, hydrogen and Oxygen, but less than 2% of nitrogen and sulfur accruing (APHA-AWWA-WPCF 1989; Jackson *et al* 1981).

Several studies have concentrated on examining the dissolved phase; for instance, dissolved aliphatic hydrocarbons have been studied by (Ooc,1975; Lysyj 1981; Ooc,1982; Burns and Roe Industrial Services 1983; Middledditch 1983; Caudle and Stephenson 1988; Brown *et al* 1990) in paraffin oils in the ranges of 606 to 2.7 mg/l .

U.S. patent no 3,581,002 suggests that hydrocarbons in water have been determined by a fluorescent method, the existence and concentration of hydrocarbon in water in low quantities of 1 ppm or greater was not easily and accurately detectable using present commercial Methods (Morrow *et al.* 1995).

1.7.1.2 Aromatics BTEX and PAHs in produced water

There is further interest in the development of particular analytical procedures to determine aromatic hydrocarbons in water samples (Zhang *et al* 1993). This is because of the toxicological properties of benzene. The dissolved hydrocarbons are dominated by the volatile aromatic fraction of the oil, normally benzene, toluene, ethyl benzene and xylene (BTEX) (Tibbetts *et al.* 1992; Brendehaug *et al.* 1992; Rabalais 1991).

Currently, several novel techniques have been developed for the analysis of BTEX and other volatile compounds in water samples such as purge-and-trap (PT) (Drozd and Novak 1979; Nunez *et al.* 1984), membrane extraction (Yang *et al.* 1994), solid-phase micro extraction (SPME) (Colombini *et al.* 2004; Criado *et al.* 2004; Zhang *et al.* 1993).and single-drop micro extraction (Sung and Huang 2005; Kaykhaii *et al.* 2005; Dong *et al.* 2005). Neff (1988) reported that the levels of polynuclear aromatic compounds in produced water were low and below toxic levels and that the smallest hydrocarbons component can be identified (Rabalais 1991), but that the higher molecular weight PAH are less water soluble (Veil *et al.* 2004).

The concentration of the 16 EPA PAHs can vary from 0.7 to 100 mg/l in produced water (Hawboldt and Adams 2005). Callaghan and Baumgartner (1990) notify that the largest quantities of aromatic compounds found were from gas condensate platforms in the North Sea. Studies which took place in Gulf of Mexico (GOM) showed that each produced water gives different result for soluble polynuclear aromatic compounds (Ooc 1982).

Volatile aromatic compounds were detected at significantly higher concentrations e.g.naphthalene, phenanthrene and dibenzothiophene (NPD) and their C1-C3 alkyl homologues, while higher molecular weight were present as chrysene and benzo(a)pyrene (Tibbetts *et al.* 1992; Roe *et al.* 1996; Rabalais 1991; Brown *et al.* 1992; Neff *et al.* 1992; Carey *et al.* 1992).

A rapid environment field monitoring tool was investigated for analysis of BTEX in water samples using portable GC–FID combined with HS-SPME. It is can be a considerable and efficient tool to examine BTEX in water samples. A preliminary evaluation of the levels of BTEX, in produced water from Guoyao, Shanghai, China has been carried out by portable GC–micro-FID (HS-SPME). Using the SPME technique the total analysis time was about 3 min as the extraction and concentration of BTEX from water needed only 1 min. Analysis time by portable GC was less than 2 min so it is a is a fast, easy and efficient tool for field analysis of BTEX in water samples (JI *et al.* 2006). On the other hand an investigation by the Alberta Research Council in 1996 identified up to 300 mg/m^3 for the 16 EPA PAHs in the emissions from the flared produced gas (Hawboldt and Adams 2005).

1.7.1.3 Acids (fatty acids) in produced water

Particular attention has focused on the acid fraction of the soluble oil in produced water (Stephenson 1992), The organic acids present are reported to be dominated by C1-C6 acids. (Tibbetts *et al.* 1992; Brendehaug *et al.* 1992). Brown *et al.* (1990) confirmed that the fatty acids in produced water occur naturally in sea water sediment arising from aquatic life, and it reported them present as sodium salts of the acids (primarily acetate sand and propionates) (Somerville 1987; Kharaka *et al.* 1986). High concentrations of simple fatty acids often exist in water produced of paraffinic oils. In contrast water from asphaltenic oils have notable amount of naphthalic acids (Stephenson 1992). The extraction of organic material from acidified produced water was done by a Freon method which is specific for the soluble organic constituents of produced water. Only small amounts of low molecular weight fatty acids were found in such extracts in early studies using gas chromatography as the acid-extractable compounds are very water soluble. This method is used due to the great variation in the weight of the Freon extract which depends on whether or not the water was acidified before analysis. (Stephenson1992). A study sponsored by the U.S. Department of Energy at Oak Ridge National Laboratory (ORNL) with Shell, Chevron, Phillips, and Statoil aimed to look at ways to manage water-soluble organics in produced water and to reduce the future production of such contaminants (Debra *et al.* 2002).

McFarlane, *et al.* (2002) characterized the actual (GOM) crude oil at high pressures in contact with produced waters and produced data to generate a predictive model for water-soluble organic content in produced waters arising from oil at high pressures which had become contaminated with water soluble organic compounds. They used a variety of analytical techniques; open column liquid chromatography was used to separate the water-soluble organic component into aliphatic, aromatic and polar fractions. Because of losses during analysis leading to a large uncertainty in the concentration data It appears unlikely that the open-column fractionation method can be used for regulatory purposes; however, only pH showed a significant effect on organic solubility in the brine. The trend of an increase in solubility with increasing pH was reproduced with a model of two-phase liquid thermodynamic equilibrium. High salinity produced water containing refractory organic pollutants was examined by Guiying *et al* (2006) using photoelectrocatalysis. The efficiency of photoelectrocatalysis decontamination of produced water was studied by both COD removal from the tested wastewater and the decrease of mutagenic activity. The results reported that the photoelectrocatalysis is slightly efficient even though the salt concentration is high. The removal efficiencies of COD when the raw produced wastewater was diluted in a 1:1 (v/v) ratio was much higher than that by photocatalytic or electrochemical oxidation individually in the photoelectrocatalytic reactor.

1.7.1.4 Phenols in produced water

The level of phenolic compounds in all oil produced water types was considerable and varied depending on the type of production gas or oil

(Stephenson 1992). Callaghan and Baumgartner (1990) reported that the largest quantities of phenols found were from gas condensate platforms in the North Sea. Jackson *et al.* (1981) demonstrated that a low recovery of phenols in produced water was obtained qualitatively by using the analytical procedures. Boitsov at el. (2007) provide an overview of the levels of the 52 known alkylphenols in produced water from nine oil installations in the North and Norwegian Seas. They verified the presence of napthas and other as yet unidentified compounds in produced water, while thiophenols were not detected since conventional GC techniques cannot achieve the desired degree of separation.

As a result of the high concentration of phenolic compounds and their high solubility in water, produced water was confirmed as being toxic to organisms (National Research Council 1985; Boesch and Rabalais 1987). However, the type of phenol and alkyl phenols that exist in produced water are degraded by bacterial and photo-oxidative processes in seawater and marine sediments .This was established in an industrial study of the soluble oil fraction of produced water by Brown *et al* (1990).

1.7.2 Salinity in produced water

Most of the studies of the salinity of the produced water showed that the produced water salinity can be higher than that of sea water ranging from 3 to 300 ppt, normal sea water Salinity is 35 ppt (Rittenhouse *et al.*1969).

The percentage of the Salinity indicated by (Hanor and Workman,1986) was between 50% and 150% in Louisiana coastal waters of the Gulf of Mexico, while in the North Slope of Alaska Costal Texas Valley of California, and Central Mississippi, U.S.A was between 18% to 320% (Kharaka *et al.* 1986).

Holstad and Johansen (2005) characterized all compounds of the produced water combining level measurement and gamma-rays (γ-rays) measurement. They studied the possibility of adding some measurements, such as, conductivity. They demonstrated that the salinity and type of salt in water are appropriate by a combination of detected scattered and transmitted radiation. They recommended that the measurement geometry and algorithms for data analysis are indispensable.

1.7.3 Heavy metals in produced water

Investigations of the levels of heavy metals in produced water have been made by both industry and government (Ooc, 1975, Jackson *et al.* 1979, Lysyj, 1981, Ooc 1982, Burns and Roe Industrial Services, 1983, Neff *et al.* 1988, SAIC 1991). The metal contents found vary widely. In Shell and NAM platforms the quantity of all metals found was very low, but variation was found when comparing fresh - condensed - water with salty formation water (Jacobs *et al.* 1993).

Heavy metals analysis has been dominated by barium and iron (Tibbetts *et al.* 1992; Neff *et al.* 1992). Most studies have found that the concentration of heavy metals in produced water is higher than metals occurring naturally in seawater (Stephenson 1992), for example heavy metals in the North Sea were value 1000 higher than of injected seawater (Jacobs *et al.*1993). However produced water has not been shown to have any adverse effect if it is discharged to the marine environment (Stephenson 1992), The samples studied in a majority of experiments contained in highest concentrations Ba, V, Ni, Zn, Cu, Cr, Cd, Hg and Pb (Rabalais 1991). For instance McCourt and peers (1988) reported that the measured alkali metals (Na, K and Li) and alkaline earth metals (Ba, Mg, Ca and Sr) in all cases applied higher concentrations, but the calcium concentration was much higher than magnesium compared to seawater. Boron, strontium and barium were found at appreciable quantities in all samples. In comparison in the samples with less or no breakthrough of seawater primarily barium content was much lower than samples from oil platform" water cut" (the ratio of water produced compared to the volume of total liquids produced), as a result of precipitation of barium sulfate scale following contact with seawater.

Samples from the GOM show the arsenic and barium levels at the highest reported concentrations. Seven platforms were analysed, while samples of produced water from the Norwegian sector of the North Sea have been reported to contain mercury and nickel (Neff 2002). Battelle (1994) and Frankiewicz *et al.* (1998) reported that 1.4 to 234 µg/l of mercury was found in the Gulf of Thailand from gas platforms. But the only metals present in produced water from two platforms from Louisiana U.S.A were barium, lead and zinc (Neff *et al* 1989, 1992).

1.7.4 Treatment chemicals in produced water

Treatment chemicals are used in the oil production as mentioned previously to treat or prevent operational problems. Production treatment chemicals include scale inhibitions. corrosion inhibitions, biocides, emulsions, gas processing chemicals, stimulation and work over chemicals (Stephenson 1992).

A sublimation method has been developed and combined with fast atom bombardment mass spectrometry (FABMS) to study surface active compounds from water (Wickbold 1966; Levsen *at el.* 1984; Righton and Watts 1986).This method was used to analyse produced waters in the platforms Murchison (block 211/19) and Hutton TLP (block 211/28) in the North Sea. The concentrated extract was analyzed by FABMS and the water spiked with demulsifier 1, scale inhibitors 1 and 2 and biocide was sublated. The technique resulted in a 500-fold reduction in the detection limit of the biocide to a more useful 10g/l, even in the presence of 20 mg/l of crude oil, but the demulsifier and scale inhibitors remained undetected. In a follow up paper tetrapentyl ammonium bromide (TPAB) was used as an internal standard on this procedure to analyse produced water (Tibbetts *et al.* 1992).

McCormack *et al.* (2001) examined oilfield produced waters and production chemicals by electrospray ionisation multi-stage mass spectrometry (ESI-MS^n). This study employed both positive and negative ion detection for the detection and characterisation of a wide range of polar and charged molecules with considerable effect. This technique was able to identify polar chemicals, such as, demulsifiers, corrosion inhibitors and biocides and identify them as imidazolines, alkylbenzene sulfonates, quaternary ammonium compounds (Quats) and ethoxylates, some observed for the first time in oilfield chemicals (OCs) and produced water. The operational use and the environmental fate of a range of OCs in oil production chemicals and produced water was confirmed by using the ESI-MS^n method coupling to liquid chromatography.

1.7.5 Radionuclides in produced water

Radionuclides in oil field production are referred to as naturally occurring radioactive material or NORM (Stephenson 1992). Stephenson (1990) indicated that until recently there have been a lot of studies considering the existence of radionuclides in produced water relying on the geological formation of where the water is produced.

This is illustrated by radionuclides studies carried out in Oklahoma, the Texas panhandle, and the GOM Coastal area studied ^{226}Ra levels ranged from 0.1 to pCi/l and ^{228}Ra levels from 8.3 to 1.507 pCi/l (Stephenson 1992). Only the concentration of uranium was determined from the effluents discharged from Shell Expro. It was below the detection limit (Jacobs *et al.* 1993).

1.7.6 Previous studies on the discharging of produced water

The effluents from the two Shell Epro and Nederlandse Aardolie Maatschappij B.V. (NAM) platforms discharged 465 tonnes dispersed oil, 251 tonnes dissolved hydrocarbons and 3909 tonnes other organics to give a total of 4625 tonnes. The relative input of polar compounds was 84% and 70 to 94 % of the soluble organic acids was acetic acid in 1989 (Jacobs *et al.*1993). Otto (1990) reported that in 1989 a study conducted by the offshore operates committee from 42 platforms in the GOM to assess the average amount of oil discharged into the environment. The study showed that 419 metric tons of oil was discharged, while in the same year in North Sea 4119 metric tons of oil discharged from 89 oil production platforms, that means an average of 46.3 metric tons per platform compared with 10.0 metric tons per platform in the GOM (Oil Industry Exploration and Production Forum 1990).

Several studies have characterized the chemical compositions of produced water all over the world, but there are very little data in the literature regarding the chemical compositions of produced water in oilfields in Libya. Libya has a large number of oil and gas fields, and produces enormous quantities of oil which are co-produced with produced water. Al Hamada oilfield is one of these fields (location 29° 30′ 86.9″N, 12° 57′ 61.0″ E). It is owned by the Arabian Gulf Company for Oil Production which is one of the Libyan national companies operating under the National Oil Corporation (NOC) of Libya. The oil production was started in 1981-82, at a rate about 27000 – 30000 barrel / day. In the face of that little work has been done on this field therefore, the purpose of this thesis is to carry out a study of the chemical composition of both organic and inorganic of produced water samples from Al- Hamada oilfield. Likewise, the thesis will investigate and analyse arrange of possible environmental pollutants, which make it necessary to propose possible remediation strategies in order to achieve safe surface disposal.

The study will provide an opportunity to play a key role in understanding any correlation between the concentrations of the certain compounds and lead to comprehensive estimation of chemical composition of produced water, and furthermore anticipate the fate and effects of the discharges of produced water to the environmental.

Chapter 2

Physical and Chemical Properties of Produced Water

2- Physical and chemical properties of produced water

Produced water is variable and can be very different from well to well. Its characteristics from oil and gas fields can also be very variable (Røe utvik 1999; Li *et al.* 2006; Cakmakce *et al.* 2008). Specifically the physiochemical composition of produced water can vary greatly (Li *et al.* 2006; Kevin and Juniel 2003) and it mainly depends on geographical location, geological formation and the type of hydrocarbons of the field and may differ from one place to another (Veil *et al.* 2004). Due to this, the salinity and the composition of the produced water may change in similar terms. This change leads to change of the density and conductivity and thereby systems based on detection of density or electrical impedance introduce drift in measurement results (Holstad and Johansen 2005).

2.1 Physical properties of the produced water

2.1.1 pH

pH value might be an important parameter and is the measure of hydrogen ion concentration (H^+) of a substance, The range of the pH in the majority of natural uncontaminated waters is between pH 6 and 9 (ASTM D 1293-99), despite that - the acidity or alkalinity can be determined at any pH of interest (ASTM D 1067-06).

Indeed reduced pH can affect the oil/water separation process and can impact on receiving waters when discharged (ASTM D 1293-99).

2.1.2- Salinity

Salinity is of major concern in onshore operations. Salinity refers to the amount of total dissolved salts (TDS) in the water. This is in reality primarily due to dissolved sodium and chloride ions along with lower levels of Ca^{2+}, $Mg^{2+}$and K^{+} (Neff 2002). Due to the high cost of the TDS analysis, it is frequently measured by electrical conductivity EC, because ions dissolved in water conduct electricity (Veil *et al.* 2004). In fact a variety of chemicals in produced water comprises inorganic salts similar to that found in sea water which makes the ocean salty (Neff 2002).The salinity and type of salt in the produced water can be determined (Holstad and Johansen 2005). Salinity concentrations can vary from very low parts per thousand (ppt) to saturation brine, from 3 to 300 ppt (Rittenhouse *et al.* 1969).

2.1.2.1 Total Dissolved Solids (TDS)

Total dissolved salts are the major constituents in produced water and the majority of these salts consist of sodium chloride. The ionic composition of these waters varies. Sodium, calcium, magnesium and potassium listed in generally decreasing concentrations are the major cations in it. However, some basins tend to have much lower median values of TDS, which is measured in parts per million or (mg/l), and the concentrations range from less than 100 ppm to over 300,000 ppm (Fillo *et al.* 1992). For example the levels of total dissolved solids in CBM areas are less than 20,000 (mg/l) (Hayes and Arthur 2004). Waters with higher TDS concentrations will be relatively conductive. Irrigation waters that are high in TDS can reduce the availability of water for plant use and also reduce the ability of plant roots to incorporate water, and reduce crop yield (Veil *et al.* 2004).

2.1.2.2 Electrical conductivity (EC)

The conductivity value is the measure of the level of soluble salts that adversely affect the growth of wide range of common agriculture plants

(Richards 1954). EC is measured in micro-Siemens per centimetre (microS /cm) (Veil *et al.* 2004). EC levels of more than 3,000 microS/cm are considered saline (All 2003). The conductivity that exceeds 3,500 microS\cm in produced water could be toxic to some of the invertebrate (ceriodaphs) (Fucik 1992).

2.1.3 Chemical oxygen demand (COD)

Chemical oxygen demand is one of the most standard water chemistry tests. The dissolved or soluble refractory organic pollutants that contribute to the high chemical oxygen demand (COD) of the water are difficult to treat (Li *et al.* 2006).

In recent years, a great deal of effort has been devoted to the development of rapid, sensitive and environment friendly methods for the determination of COD (Li *et al.* 2006).The COD in oilfield wastewater is usually still high (Lu *et al.* 2006).This indicates that the produced water contains numerous dissolved organic pollutants (Li *et al.* 2006).The identification of components that contribute to COD is very important in assessing the efficiency of the wastewater treatment process and removal technology (Lu *et al.* 2006).

Produced water from offshore oil wells contains various type of salts, and typical contents of ions for formation water and seawater are as listed in Table 4 (Holstad and Johansen 2005).

2.2 Chemical properties of produced water

2.2.1 Cations and anions

The cations in produced water are atoms or molecules that have gained a positive charge like H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, and Fe^{3+}. The primary components of water hardness which can cause pipe or tube scaling are calcium and magnesium salts which frequently cause failures and loss of process efficiency due to clogging or loss of heat transfer. Other salts are present in trace amounts (ASTM D 1126-02).

Sodium salts are very soluble in water and if the ratio of sodium to calcium is high, it will be harmful to soil structure (ASTM D 4191-79).The use of sodium salts is common in industry; therefore, many industrial wastewaters contain significant quantities of sodium. For high-pressure boiler feed-water even trace amounts of sodium are of concern.

In contrast an anion is an atom or molecule that has a negative charge. Anions are abundant in seawater and hard water like OH^-, Cl^-, S^{2-}, HCO_3^-, CO_3^{2-} and SO_4^{2-}.

The amount of the chloride ion present in produced water must be measured accurately as its concentration is regulated (ASTM-D512-89). The concentration of sulfate in produced water is highly variable and is lower than that of the seawater (Neff 2002).

The water molecule, like a magnet, is polar and has positive and negative ends. Water molecules can reduce the attraction between the cation and anion. This is what happens to table salt, NaCl, in water.

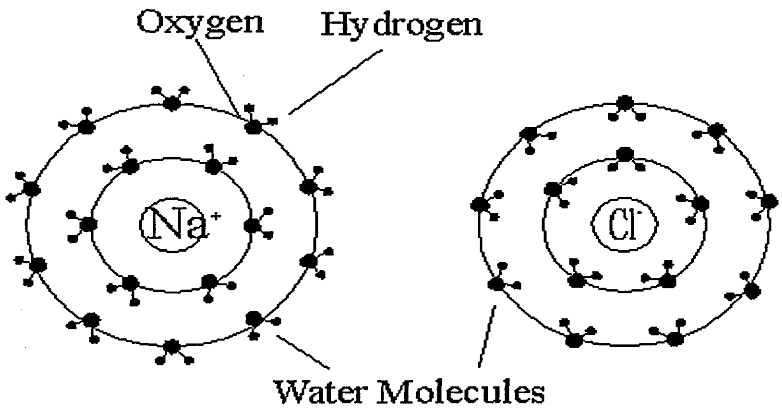

Figure 2.1 NaCl salt in water

2.2.2 Sodium adsorption ratio (SAR).

Sodium adsorption ratio (SAR) is a measure of the relative proportion of sodium cations to other cations in total dissolved solids. SAR is the standard measure of sodicity. Also it is a parameter used for determining the suitability of water for irrigation purposes. High sodicity affects soil, the higher the SAR, the greater the potential for reduced permeability, which reduces infiltration, reduces hydraulic conductivity, and causes surface crusting. Irrigation waters with SAR levels greater than 12 are considered sodic (All 2003).SAR is a calculated parameter that relates the concentration of sodium to the sum of the concentrations of calcium and magnesium.

The SAR is calculated using the following formula:

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{++} + Mg^{++}}{2}}}$$

The values for sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) in this equation are expressed in units of milli-equivalents per litter (meq/l). Most monitoring data will typically be reported in terms of (mg/l), which must be converted.

The conversions are:

$$\text{meq/l} = \frac{\text{Equivalent weight in mg / meq}}{\text{Concentration in mg / l}}$$

Charge:

Na^+ = 23.0 mg/meq (atomic weight of 23, charge of 1)

Ca^{2+} = 20.0 mg/meq (atomic weight of 40.078, charge of 2)

Mg^{2+} = 12.15 mg/meq (atomic weight of 24.3, charge of 2)

2.2.3 Suspended solids

Dissolved or suspended solids, produced solids such as sand or silt, and recently injected fluids and additives that may have been placed in the formation as a result of exploration and production activities are also important in produced water (GodshalL 2006).

Filterable and non-filterable solids are important in the treatment of both raw and waste water, and in the monitoring of streams. Waste solids impose a suspended and settleable residue in receiving waters, that provide a matrix for some biological substances and, in sufficient quantity, damage respiration of organisms (ASTM D 5907-96). In order to illustrate these properties of produced water data for ions in the Vakeflar and Devecatagi well are shown in Table 2.1 and in oil field brines and seawater in table Table 2.2.

Table 2.1 Properties of ions in raw produced water of the Vakeflar and Devecatagi well (Cakmakce *et al.* 2008).

Parameters (mg/l)	Vakflar		Devecatagi			Standard Values in TWPCR for petroleum industry
	June 2005	July 2006 ITU	June 2005 Unmixed sample	June 2005 Settled sample	July 2006 ITU	
BOD	7000	-	-	-	-	-
COD	24,500	1681	3480	–	588	250
SS	35,830	–	606	132	–	100
NH4	2.4	–	14.5	–	–	10
Phenol	10	–	0.59	–	–	1
CN^-	<0.01	–	0.005	–	–	0.5
Oil and grease	1565	–	472	–	–	10
Total salinity %	–	7.2	8.2	–	7.13	
Free chlorine	<0.02	–	–	–	–	
pH	7.85	7.8	7.87	–	7.1	6-9
Conductivity µS/cm	–	18.8	14.3	–	47.6	
Na^+	3165	4480	4096	–	18.9	200
Cl^-	–	3199	4004	–	16.7	
$SO4^{2-}$	355	–	390		–	1700
Cd	<0.15	–	0.001	0.001	–	0.1
Co	–	–	–	–	–	
Cr	1.75	–	–	–	–	
Cu	0.98	–	0.01	0.002	–	0.5
Fe	30	–	1.63	0.25	–	8
Ni	–	–	0.004	0.004	–	
Zn	2.22	–	0.001	0.001	0.225	0.5
Pb	0.52	–	0.006	0.003	–	0.5
Alkalinity $CaCO_3$	–	–	–	–	–	
Total sulfate	1.7	–	13.6	–	–	

Table 2.2 Typical contents of ions in oil field brines and seawater (Wright *et al* 1994; Barlow 2003).

Ions	Formation water (mg/l)	Sea water (mg/l)
Sodium Na^+	30730	10500
Potassium K^+	710	390
Magnesium Mg^{2+}	470	1350
Chloride Cl^-	59640	19000
Calcium Ca^{2+}	5300	410
Barium Ba^{2+}	420	<1
Strontium Sr^{2+}	840	8
Sulfate SO^{4-}	4	2700

2.3 Sampling

The produced water samples used in this study were collected from the AL-Hamada oilfield in the Libyan Arab desert (Figure 2.2)

The samples were taken from four points:

S1 - Main stream

S2 - Main storage tank of crude oil

S3 - Separator

S4 - The pit of produced water disposal

Photographs of sampling points S1 to S4 are shown in Appendix B

The methods of collection and sample size were chosen to ensure that the samples obtained are representative of the environment from which it they have been taken. They were taken in a way to avoid introduction of bias systematic or non-systematic errors and stored at 4 °C in darkness until used.

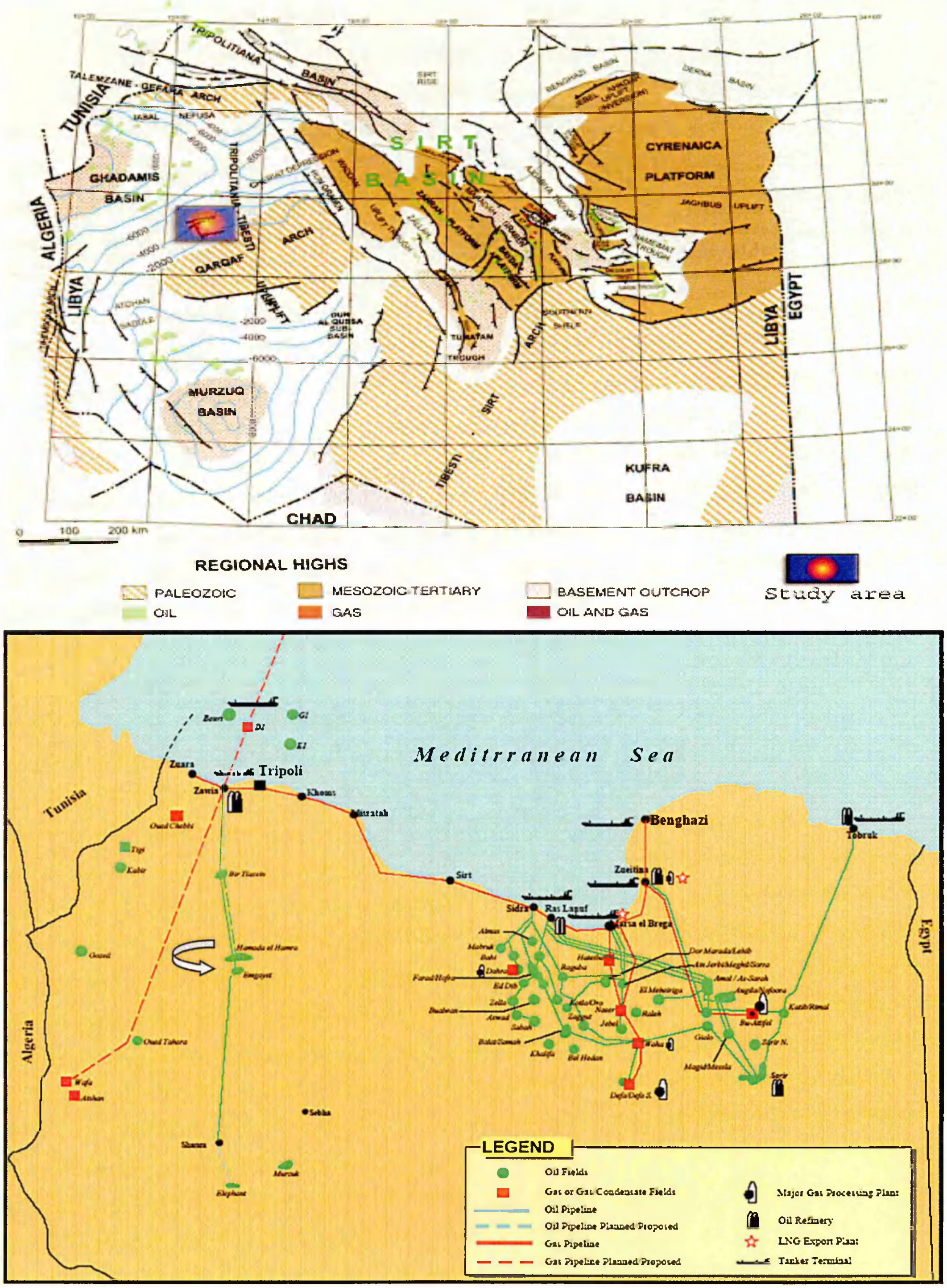

Figure 2.2 Location map (29° 30′ 86.9″N, 12° 57′ 61.0″ E) of the AL-Hamada oilfield (Rusk, 2001; Abadi, 2005).

2.4 Materials and methods:

2.4.1 Standard preparation of glassware and chemicals used

All glassware used in this study were scrupulously cleaned they were washed with soap and rinsed with tap water prior to drying, followed by detergent washing by rinsing with acetone and the appropriate solvents before being left to air dry, in addition chemicals used in this study were all analytical grade reagents. All reagents were used without further purification.

2.4.2 Physical properties

2.4.2.1 pH Measurement

The test must be performed immediately after the receipt of water sample in the laboratory, this due to the fact that it is subjected too much interference as Sedimentation, oxidation and hydrolysis.

2.4.2.1.1 Instrumentation and method used

The pH values were measured using a glass electrode connected to a Knick digital pH meter 646, (Berlin, Germany) as direct reading. The instrument was standardized with three singlet pH buffer solution (pH 4, pH 7 and pH 10 respectively) Germany HACH company headquarters. The temperature of the solution was entered digitally before the pH of the sample was measured according to the standard method ASTM D (1293- 99).

2.4.2.1.2 Procedure

The pH of the sample with the same temperature as the buffer solution was measured by putting the sample and the electrode in to the glass beaker, whilst stirring the pH value taken when there was no fluctuation observed. Then the electrode was rinsed with de-ionized water and dried after that immersed into buffer solution.

2.4.2.2 Salinity

The salinity was calculated as NaCl (mg/l) (Cations + Anions)

Table 2.3 Conversion factors for calculating salinity

Ion		Factor of conversion	Equivalent salinity ppm
Calcium	Ca^{2+}	0.95	Equivalent NaCl
Magnesium	Mg^{2+}	2.00	Equivalent NaCl
Sodium	Na^{+}	1.00	Equivalent NaCl
Bicarbonate	HCO_3^{-}	0.27	Equivalent NaCl
Carbonate	CO_3^{2-}	1.26	Equivalent NaCl
Chloride	Cl^{-}	1.00	Equivalent NaCl
Sulfate	SO_4^{2-}	0.50	Equivalent NaCl

The summation of all the converted ions into the equivalent amount of sodium chloride gives the total equivalent salinity, NaCl, concentration.

2.4.2.2.1 Total Dissolved Solids (TDS) measurement

TDS are dissolved substances which remain after evaporation of the water, at fixed temperature which is usually 180˚C, and that passed through a standard glass filter.

The chemical composition of the water has a marked effect on the TDS obtained.

2.4.2.2.1.1 Method used

TDS was measured according to ASTM D 5907-96 a

2.4.2.2.1.2 Procedure

A 0.45-µm filter was inserted in the membrane filter assembly, and then the vacuum was applied .The disc was washed three times with 90 ml of de-ionized water. 100 ml of the sample was filtered slowly and washed with 20 to 60 ml of de-ionized water and complete drying between washings was allowed. The filtrate aliquot was transferred to the 125 ml glass weighed evaporation dish that heated close up 180°C over a water bath and evaporated until dryness. The evaporation dish was dried for 1 h at 180°C in the oven, and then allowed to cool down in a desiccator for 30 minutes prior to weighing. TDS was calculated by weighing as shown below:

$$\text{PPM (TDS)} = \frac{(A-B) \times 1000}{S \text{ (volume)}}$$

Where A = weight of residue + weight of dish (mg)

B = Weight of dish (mg)

S = Sample Volume (ml)

2.4.2.2.2 Electrical conductivity (EC) measurement

The E.C is a function of temperature where the ionic velocities increase with the increase of temperature, and consequently the conductivity increase of a value approximately 2% per degree centigrade .Due to this fact the E.C is always reported with respect to temperature of 25 °C.

2.4.2.2.2.1 Instrument and method used

The electrical conductivity was measured by Conduktometer type LF 191. This was calibrated by using reference standard solution (12880 mS/cm HANNA Instruments, Italy) at 25 ˚C, and was measured according to the Standard Method D 1125 – 95 (Re-approved 2009).

2.4.2.2.2.2 Procedure

The conductivity cell was rinsed with de-ionized water and filled with calibration standard. Then the conductivity was read and recorded after which the cell was rinsed with de-ionized water and filled with the sample. Then the conductivity was read and recorded.

2.4.2.3 COD Measurement

2.4.2.3.1 Method used

COD was determined using the potassium dichromate following the procedures described in the standard method ASTM D 1252 – 06 Test method A

2.4.2.3.2 Reagents used

Reflux apparatus, ferrous ammonium sulfate solution (0.25 N), ferrous ammonium sulfate solution (0.025 N), phenanthroline ferrous sulfate indicator solution, potassium acid phthalate solution, standard (1 ml = 1 mg COD) and potassium dichromate solution, standard (0.025 N). The use of concentrations in terms of normality (N) is still common in ASTM standard methods and so will be used here without conversion.

2.4.2.3.3 Procedure

50.0 ml of the mixed sample was placed in a reflux flask in an ice bath, then 1 g of powdered mercuric sulfate and 5.0 ml of concentrated sulphuric acid was added. Afterwards, 25.0 ml of 0.25 *N* standard potassium dichromate solution and some glass beads were added. Then the mixture was stirred vigorously below 40°C while 70 ml of sulphuric acid-silver sulfate solution was added. The mixture in the flask was joined to the condenser which covered by small beaker and cold water was flowing, then heated for 2 h. The condenser was washed with 25 ml of water and the flask was diluted to 300 ml with de-ionized water. After cooling to room temperature, 8 to 10 drops of phenanthroline ferrous sulfate were added to the solution and titrated with 0.25 *N* ferrous ammonium solution until the colour was changed from a blue-green to a reddish hue. A blank was prepared in the same manner.

Calculation

COD is calculated as shown below:

$$\text{COD, (mg/l)} = ((A - B)\ N \times 8000)/S$$

Where:

A = ferrous ammonium sulfate solutions required for titration of the blank (ml)

B = ferrous ammonium sulfate solution required for titration of the sample (ml)

N =normality of the ferrous ammonium sulfate solution,

S =sample used for the test (ml).

2.4.3 Chemical properties

2.4.3.1 Cation and anion measurements.

Hardness is expressed as calcium carbonate .This mineral is almost insoluble in distilled water, but if any water contains carbonate. This contributes to dissolve the calcium or magnesium carbonate according to the following reaction

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

$$Mg\,CO_3 + H_2O + CO_2 \longrightarrow Mg(HCO_3)_2$$

2.4.3.1.1 Instrument and method used

Cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+})

Sodium (Na^{+}) and potassium (K^{+}) were analyzed by flame emission. (Flame Photometer corning 400, Corning Medical & Scientific, England UK)

Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were measured by titration according to Standard Method ASTM D 511- 93(reapproved 1998).

Total hardness, calcium and magnesium hardness

$CaCO_3$ (mg/l) was measured by titration with EDTA according to ASTM Standard Method D 1126 – 02 (Reapproved 2007).

Anions (HCO_3^{-}, CO_3^{2-}, Cl^{-}, SO_4^{2-})

Carbonate (CO_3^{2-}) /bicarbonate (HCO_3^{-}) were measured by titration with standard acid according to standard Method **D 1067 – 06.**

Chloride ion was determined using the silver nitrate titration method following ASTM D4458 – 09.

Sulfate SO_4^{2-} was measured using ASTM D 516-68.

2.4.3.1.2 Procedures

Cations (Ca^{2+}, Mg^{2+}, Na^+, K^+)

Calcium Ca^{2+}, magnesium Mg^{2+}

As the specific gravity of the sample was between1.000 and 1.025, 25 ml of filtered sample were pipetted into a 150 ml beaker and the pH was adjusted to pH 7 and to pH 10 with ammonium hydroxide (NH_4OH, sp gr 0.900). While the sample was stirred, 1 ml of $NH_2OH{\cdot}HCl$ solution (30 g of hydroxylamine hydrochloride in water to 1000 ml), 1 ml of buffer solution (the pH range 10.0) and 2 ml of NaCN solution(25 g of sodium cyanide in water to 1000 ml) were added . Then a small amount of $K_4Fe(CN)_6{\cdot}3H_2O$ and 4 to 5 drops of Chrome Black T indicator were added. The sample aliquot was titrated with EDTA solution until the color changed to clear blue and after 5 min the volume of EDTA solution required to titrate calcium plus magnesium was recorded. A reagent blank was titrated following the similar steps that have been followed in respect of calcium plus magnesium.

Calcium Ca^{2+}

25 ml of filtered sample was pipetted into 150ml beaker then 1 ml of $NH_2OH{\cdot}HCl$ and 1 ml of NaOH solution were added and the pH was adjusted to pH13. After adding 1ml of NaCN and 0.2 g of calcium indicator solution (fluorescein methylene iminodiacetic acid), the sample aliquot was titrated with standard EDTA, and the titration continued till the color was changed from deep green to purple. After 5 min of the titration the end point was

recorded (volume of EDTA solution required to titrate calcium). A reagent blank correction was determined following the similar steps to that used to calcium titrate.

Calculations

Calcium mg/ l = $(A \times B / D) \times 40\,100$

Magnesium mg/ l = $\{(C \times B / E) - (A \times B / D)\}\ 24300$

Where:

A = (EDTA standard solution required to titrate calcium in the sample) – (Volume of EDTA consumed in titrating reagent blank correction).

B = Molarity of EDTA standard solution,

C = EDTA standard solution required to titrate ca^{2+} Mg^{2+} in the blank correction

D =sample taken ml, to measure Ca^{2+}

E = sample taken to measure Ca^{2+} and Mg^{2+}

Total hardness as $CaCO_3$ (mg/l)

100 ml of the sample was transferred into 200 ml glass beaker and 1 ml of buffer solution (NH_4OH) was added to adjust the pH of the sample to pH 7 and pH 10. Then 0.4 g of hardness indicator powder was added, after which the mixture was stirred and titrated with Na_2H_2 EDTA solution till the color changed from red to blue. After 5 min of titration the end point was recorded.

Calculation

Hardness (mg/l) as $CaCO_3$= 1000 C/S

Where

C = Volume, ml of Na_2H_2 EDTA used for titrating

S = sample Volume, ml

Calcium hardness as $CaCO_3$ (mg/l) and magnesium

Hardness as $CaCO_3$ (mg/l)

50 ml of the sample was transferred into 200ml glass beaker then 2ml of NaOH solution and 0.2 g of calcium indicator were added. Then the mixture was titrated with Na_2H_2 EDTA solution with continues stirring till the color was changed from red to royal blue and after 5 min from the start of the titration to the end point was recorded

Calculation

Calcium Hardness (mg/l) as $CaCO_3$= 1000 D/S

Where D = Volume, ml of Na_2H_2 EDTA used for calcium hardness titrating

S = sample Volume, ml

Magnesium Hardness = (Hardness (mg/l) - Calcium Hardness) (mg/l) as $CaCO_3$.

Potassium, sodium

A blank and sodium calibration standards containing 5, 10,100 ppm of sodium were prepared. The emission was deduced using the flame photometer starting from highest concentration and working towards the most diluted. Potassium was measured in the same way with standards 2, 5, 10 ppm of K^+; their concentrations were deduced from the calibration curve of the standard solutions.

Anions (HCO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-)

Carbonate CO_3^{2-}, **bicarbonate** HCO_3^-

100 ml of the sample was transferred into 300-ml glass beaker at room temperature and gently titrated to the end point with 0.02 M H_2SO_4 in the presence of 3 drops of phenolphthalein as an indicator solution (5 g/l) and stirring was continued while the titration was in progress. The color did not change which meant that the sample did not contain carbonate.

Bicarbonate was determined by following the same steps in respect of carbonate. 0.5ml Methyl orange indicator solution was used and the end point recorded when the colour was changed from pink-yellow to pink-orange.

Calculation Cl^-

$$\text{meq/l of } HCO_3^- = \frac{\text{B (Volume end point)} \times \text{N } H_2SO_4 \times 1000}{\text{Sample Volume, ml}}$$

$$\text{meq/l of } HCO_3^- \times \text{MW (61)} = \text{ppm}$$

Chloride (mg/l)

The sample was filtered and transferred to 150 ml conical flask and diluted with 100 ml water. 1 g of sodium bicarbonate was added and stirred and the pH was adjusted to 6.5 and 8. 0. 1 ml of 5 % chromate indicator was used as an indicator while titrating with 0.141 N silver nitrate solution. The titration was continued until the colour was changed to a permanent orange colour preceding the brick red colour precipitate.

Calculation

$$\text{mg Cl / l} = \frac{\text{ml } (AgNO_3) \text{ used- B x T x 1000}}{\text{Vol of sample}}$$

Where T = titer, mg Cl^-/ml of $AgNO_3$, and

B = indicator blank.

Sulfate SO_4^{2-}

The sample was filtered through a 0.45-μm filter paper. The acidity of 200 ml of the filtered sample was adjusted to methyl orange end point and 10 ml excess of 10 % HCl was added. The acidified solution was heated to boiling and 5 ml of hot $BaCl_2$ solution was added while stirring vigorously.

The temperature was kept below boiling until the liquid became clear and the precipitate was allowed to settle completely for 2h .The suspension of BaSO4 was filtered on fine ashes filter paper and the precipitate was washed with hot water until the washing was free of chlorides as indicated by testing the last portion of the washing with $AgNO_3$ solution. The filter paper and the contents were placed in a weighed platinum crucible and charred without flaming. The residue was ignited at about 800 °C for 1 h, after which few drops of H_2SO_4 and HF were added and the solution was evaporated in a hood to expel silica as SiF_4 .The residue was ignited at about 800 °C, cooled in a desiccator and the $BaSO_4$ weighed.

Calculation

$$\text{Sulfate, mg/l} = \frac{W \times 411.5000}{\text{Vol of sample}}$$

Where W = grams of $BaSO_4$

2.5.2.2 Sodium adsorption ratio (SAR)

SAR was calculated using the following equation:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{++} + Mg^{++}}{2}}}$$

2.5 Results and discussion

2.5.1 Results

It was found that produced water contains a complex matrix of organic and inorganic materials which is similar those in crude oil and natural gas. The basic components can therefore be grouped into the following main categories oil heavy metals, radionuclide chemical salt and dissolved oxygen.

The physical -chemical properties of produced water from Al Hamada oilfield were measured to characterize the pollutants contained within it..

2.5.1.1 The physical properties

The physical properties are summarized in Table (**2.4)** and Figures (**2.3 to 2.9)**; showing the pH, resistivity, salinity calculated as NaCl (mg/l), electrical conductivity, dissolved solids as evaporated total dissolved solids, TDS (calculated) and COD (mg/l).

Table 2.4 pH, Conductivity EC, resistivity, salinity as NaCl, TDS, COD

Sample No	**S1**	**S2**	**S3**	**S4**
pH – value	7.60	7.66	7.78	7.66
Salinity calculated as NaCl (mg/l)	1.3	1.2	1.2	1.2
Resistivity ohm/m@20°C	4.3	4.2	4.1	4.2
Conductivity µS/cm@25°C	2.3	2.4	2.4	2.4
Dissolved Solids evap @180°C (mg/l)	1.7	1.5	1.5	1.5
Total Dissolved Solids (calculated) (mg/l)	1.7	1.5	1.5	1.5
COD (mg/l)	0.80	0.27	0.36	0.12

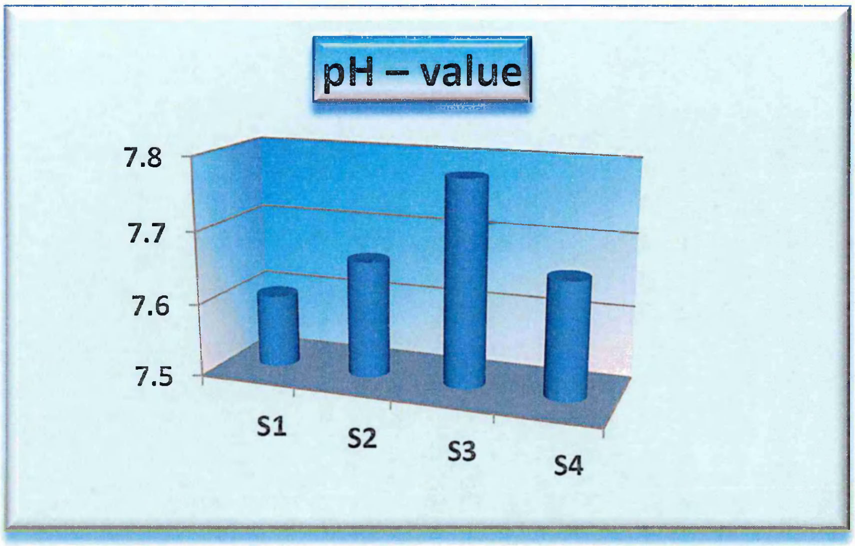

Figure2.3 pH Values of produced water samples

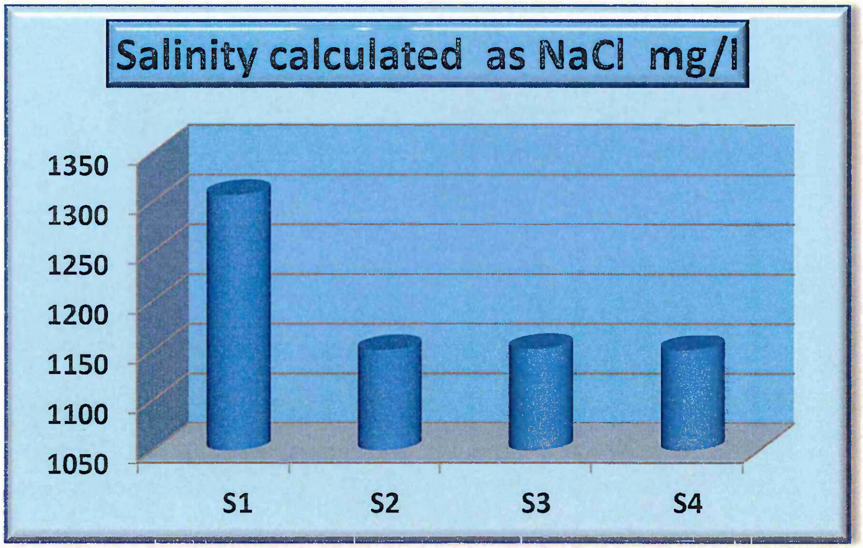

Figure2.4 Salinity calculated as NaCl (mg/l) in produced water samples

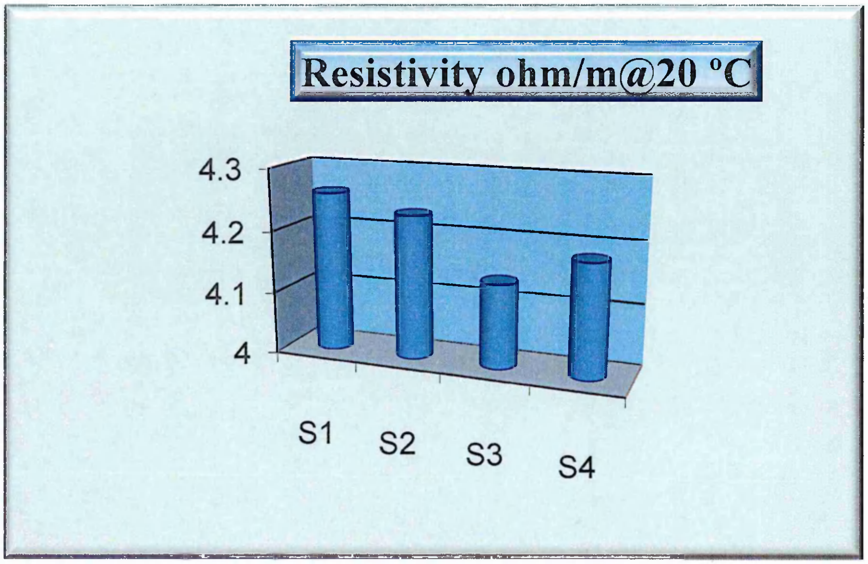

Figure 2.5 Values of resistivity in the produced water samples

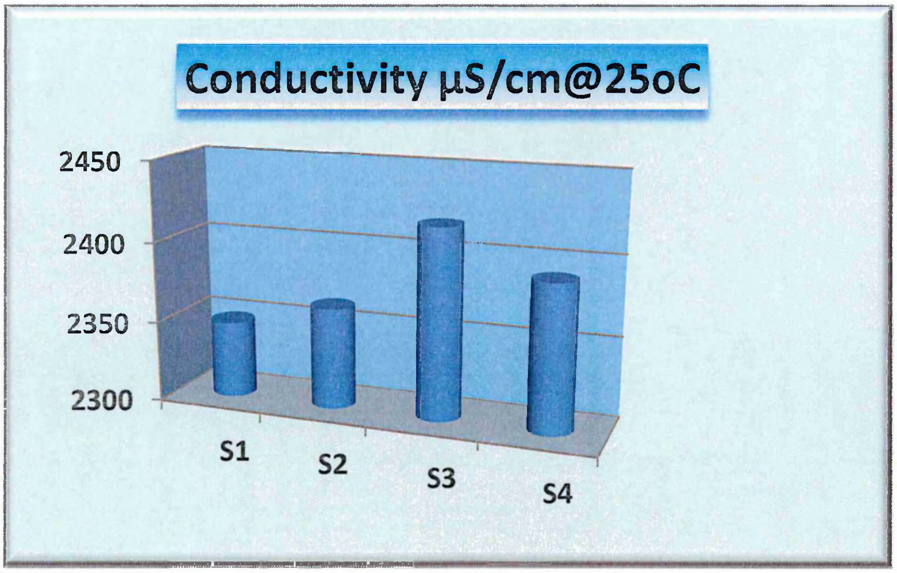

Figure 2.6 Values of electrical conductivity in the produced water samples

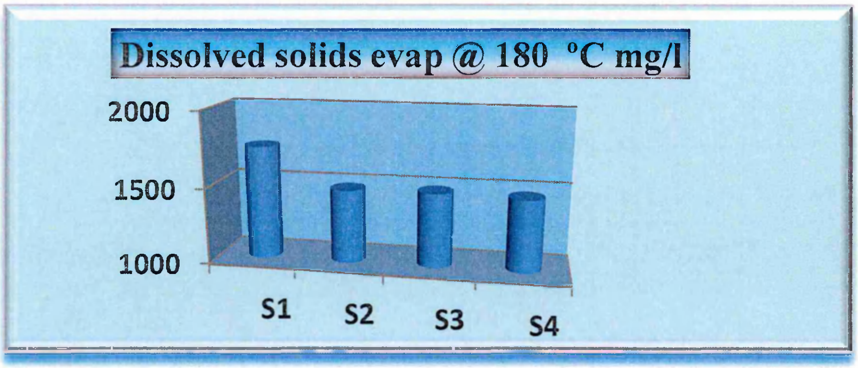

Figure 2.7 Concentrations of Total Dissolved Solids (TDS) in the produced water samples @180°C

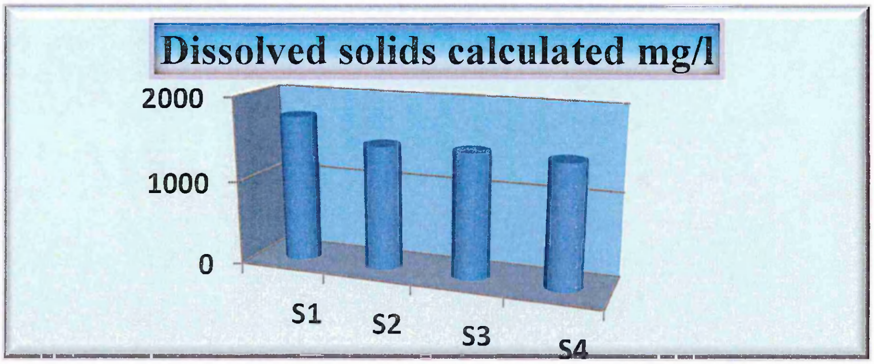

Figure 2.8 Concentration of Total Dissolved Solids (TDS) in the produced water samples

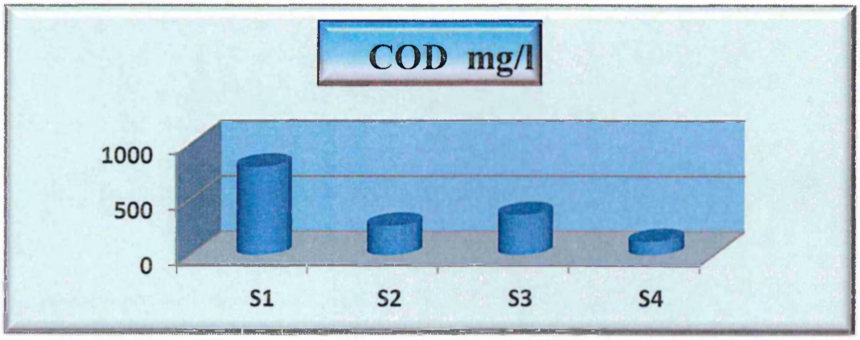

Figure 2.9 Chemical oxygen demand (COD) (mg/l) of the produced water

2.5.2.1 Chemical composition

Group 1

The concentration of cations (mg/l) calcium, magnesium, potassium, sodium)

Total hardness as $CaCO_3$ (mg/l), calcium hardness as $CaCO_3$ (mg/l), magnesium hardness as $CaCO_3$ (mg/l), methyl orange alkalinity as $CaCO_3$ (mg/l), are presented in Tables 2.5 and 2.6 and are shown in Figures **2.10 to 2.17**.

Table 2.5 Cations (mg/l) (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+})

Sample No	S1	S2	S3	S4
Ca^{2+}	60	68	100	64
Mg^{2+}	34	53	44	63
K^{+}	64	59	60	59
Na^{+}	398	296	273	270

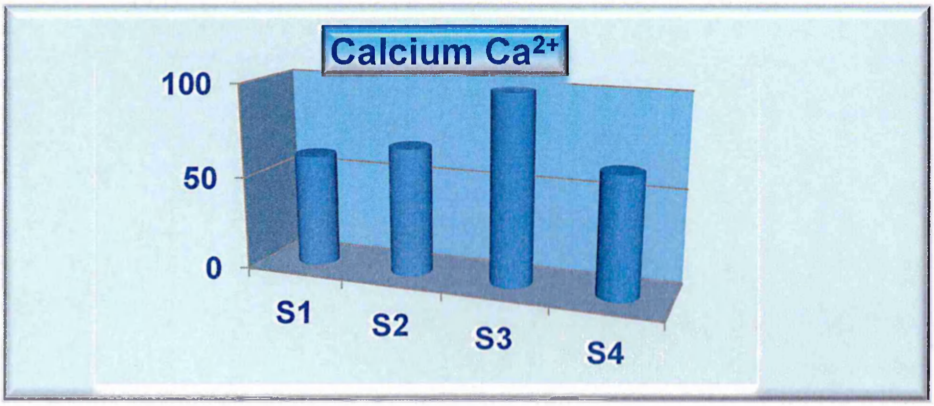

Figure 2.10 Concentrations of Ca^{2+} (mg/l) in produced water samples

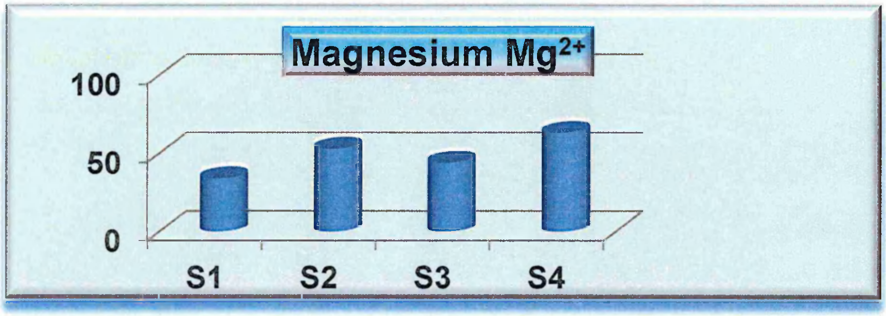

Figure 2.11 Concentrations of Mg^{+2} (mg/l) in produced water samples

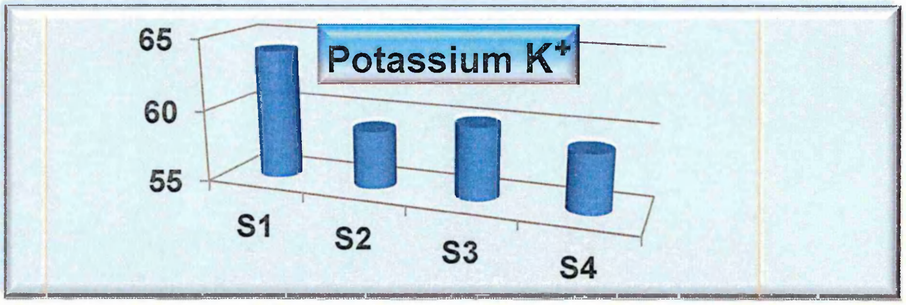

Figure 2.12 Concentrations of K^+ (mg/l) in produced water samples

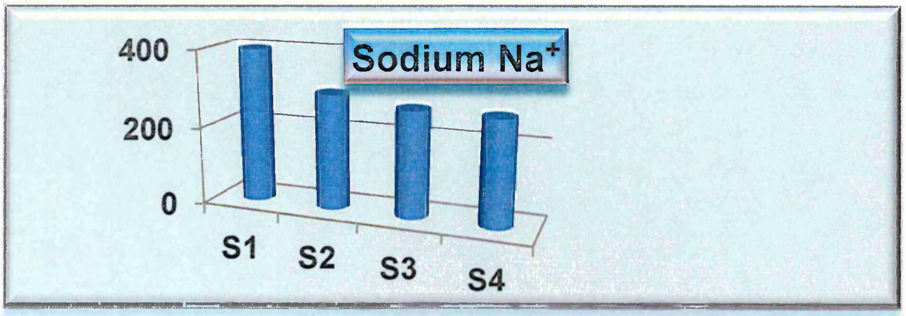

Figure2.13 Concentrations of Na^+ (mg/l) in produced water samples

Table 2.6 Total hardness, calcium and magnesium hardness, methyl orange alkalinity as $CaCO_3$ (mg/l)

Sample No	**S1**	**S2**	**S3**	**S4**
Total hardness as $CaCO_3$	290	390	430	420
Calcium hardness as $CaCO_3$	150	170	250	160
Magnesium hardness as $CaCO_3$	140	220	180	260
Methyl orange alk.as $CaCO_3$	298	470	417	420

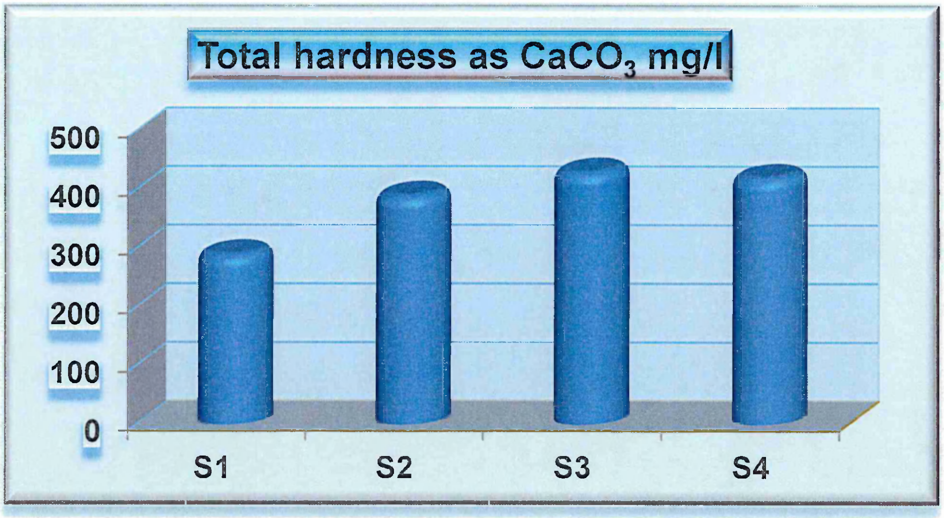

Figure 2.14 Concentration of total hardness as $CaCO_3$ (mg/l) in produced water samples

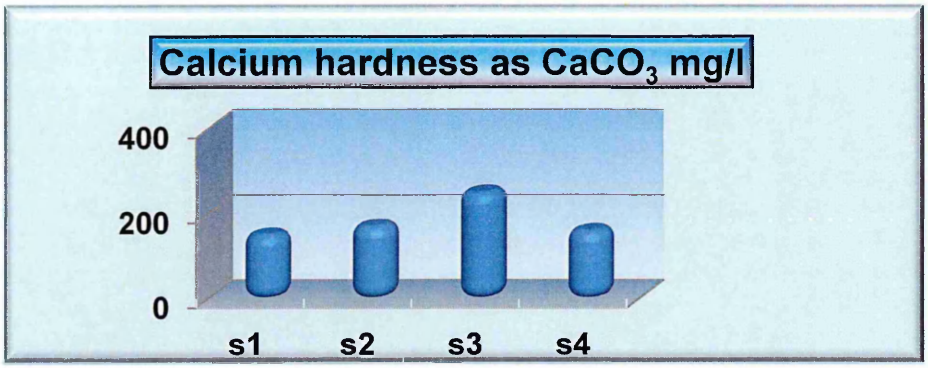

Figure 2.15 Concentration of calcium hardness as $CaCO_3$ (mg/l) in produced water samples

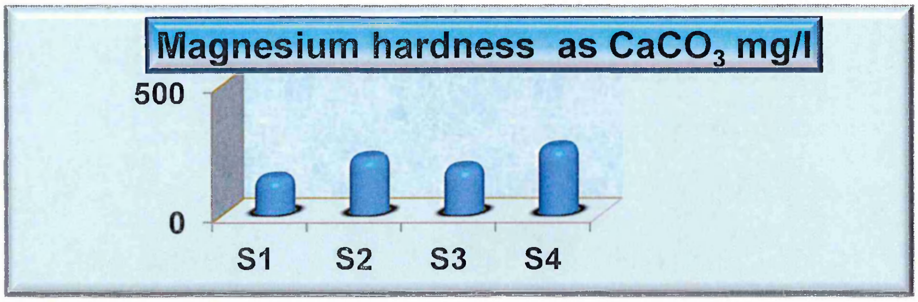

Figure 2.16 Concentrations of magnesium hardness as $CaCO_3$ (mg/l) in produced water samples

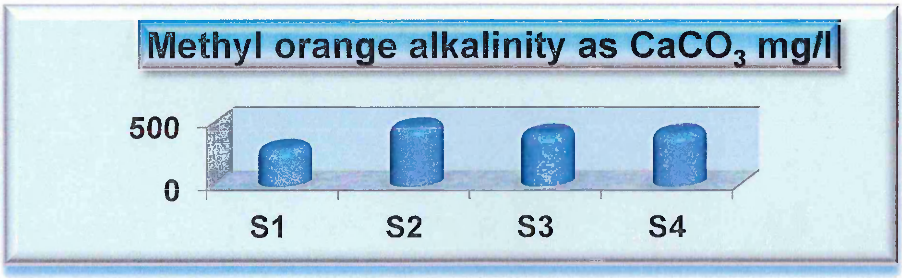

Figure 2.17 Concentration of methyl orange alkalinity as $CaCO_3$ (mg/l) in produced water samples

Group 2

The concentration of the anions (mg/l) chloride, bicarbonate, and sulfate are given in the Table 2.7 and shown in Figure **2.18, 2.19** and **2.20**

Table 2.7 Anions Cl^-, HCO_3^-, SO_4^{2-}

Sample No	**S1**	**S2**	**S3**	**S4**
Cl^- (mg/l)	442	479	452	455
HCO_3^- (mg/l)	364	391	387	390
SO_4^{2-} (mg/l)	360	125	160	150

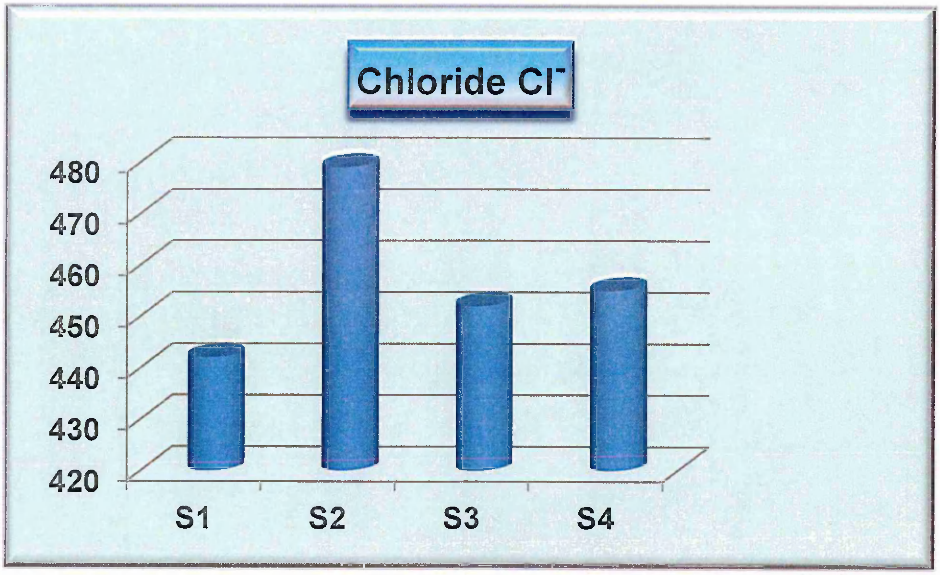

Figure 2.18 Concentrations of Cl^- (mg/l) in produced water samples

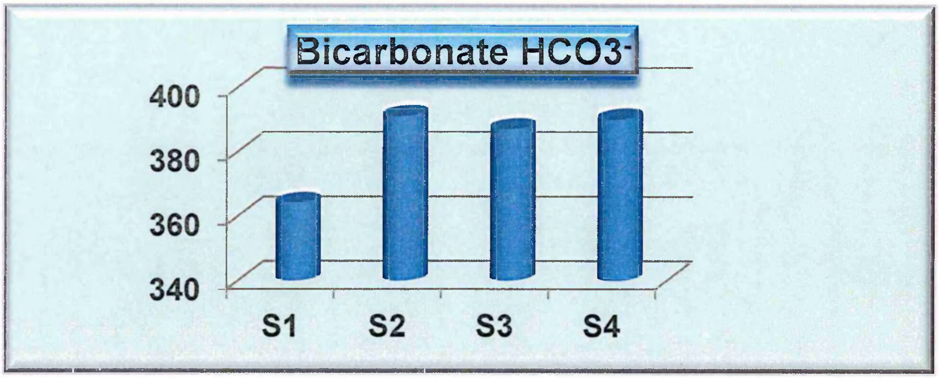

Figure 2.19 Concentrations of HCO_3^- (mg/l) in produced water samples

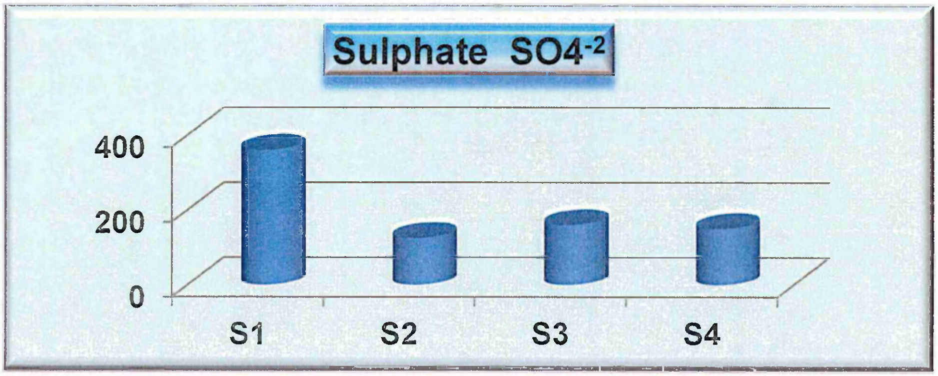

Figure 2.20 Concentrations of SO_4^{2-} (mg/l) in produced water Samples

Sodium adsorption ratio (SAR).

Table 2.8 Sodium adsorption ratio

Sample No.	S1	S2	S3	S4
SAR	58	38	32	34

2.5.2 Discussion:-

Produced water is considered to be an important source of environmental pollution due to the foreign matter carried by it, since this is toxic and negatively impacts on the environmental ecosystem. A series of chemical tests were carried out in order to identify and assess the impact of produced water from the AL-Hamada oilfield in the Libyan Arab desert on the environment and to propose the proper measures to deal with it.

2.5.2.1 Discussion of the physical properties

2.5.2.1.1 pH

The pH results presented in Figure 2.3 show that pH values of all samples are nearly constant but that there was a slight increase in sample 3. These pH values are considered to be within the accepted limits 6-9, considering that the pure distilled water has a pH measurement of 7.

2.5.2.1.2 Salinity calculated as NaCl (mg/l)

The salinity declined sharply from sample 1 to the other samples after which it remained nearly constant; in contrast it decreased slightly from sample 3 to 4, as shown in Figure 2.4.

2.5.2.1.2.1 Electrical conductivity (EC) µs/cm@25oC

The EC and TDS are a good indication of the salts present in the water and are considered to be at a normal level and not forming a threat.

EC and TDS data are shown in Figure 2.6 EC increased gradually from sample 1 to sample 3 after which fall relatively. EC values varied between 2348 to 2418 µS/cm. These values might be considered to be close to the limit of 4000 µS/cm, granted that normal potable water has an average conductivity of 1000 to 1500 µS/cm, where All (2003) indicated that EC levels of more than 3000 µs /cm are considered saline.

2.5.2.1.2.2 Dissolved Solids (evap) & Total Dissolved Solids (calculated)

As shown in the Figures 2.7 and 2.8 dissolved solids (evap) and total dissolved solids (calculated) fall sharply from sample 1 to 2 and then decline from sample 2 to 4.The amount of the TDS was found in all samples to be within the accepted range of TDS in produced water which ranges from 100 to over 300,000 ppm.

2.5.2.1.3 COD (mg/l).

Figure 2.9 shows that there was a dramatic decrease in COD from 795.6 to 265.2 between sample 1 and 2 then a moderate increase between sample 2 and 3 after which it felt to the lowest point for sample 4. The COD values for all samples were within the expected range in produced water which is approximately 1000 ppm due to the oil water separation and gas flotation.

2.5.2.2 Discussion of chemical properties:

2.5.2.2.1 Cations and anions

Figures 2.10 to 2.13 show the concentrations of cations and anions. Cation concentration ranges were as follows Ca^{2+} 60 -100' Mg^{2+} 34 - 63, K^+ 59 - 64 and Na^+ 270 - 398 all values (mg/l), and in the Figures 2.18 to 2.20 the anions vary between Cl^- 442 - 479, HCO_3^- 387 - 391, SO_4^{2-} 125 -366)

Waters high in chloride are also high in sodium, which are completely dissolved in water in the form of sodium chloride. However; the cation and the anion values are generally considered to be low and do not form any toxic threats or effect the environment negatively.

2.5.2.2.2 Total hardness as $CaCO_3$ (mg/l).

Figure 2.14 shows a considerable increase in total hardness as $CaCO_3$ from sample 1 to 2 then an increase gradually between sample 2 and 3 after a slight decrease.

2.5.2.2.3 Calcium hardness as $CaCO_3$ (mg/l).

The concentration changes in the calcium hardness as $CaCO_3$ was small between samples 1 to 2 but it increased dramatically to sample 3 and then decreased considerably from sample 3 to 4 as shown in Figure 2.15.

2.5.2.2.4 Magnesium hardness as $CaCO_3$ (mg/l).

It can be seen in Figure 2.16 that magnesium hardness as $CaCO_3$ rose steadily from sample 1 to 2 and 3 to 4 but dropped relatively between samples 2 and 3.

2.5.2.2.5 Methyl orange alkalinity as $CaCO_3$ (mg/l).

Figure 2.17 shows that the methyl orange alkalinity as $CaCO_3$ between the samples varies.

2.5.2.2.6 Sodium adsorption ratio (SAR)

Table 2.8 shows the results of the sodium adsorption ratio which is calculated from the cationic distributions. These values are greater than 12 so the produced water is considered sodic (high in sodium Na^+), the high concentration due to decomposition of large amounts of bacteria in that area.

2.6 Conclusions

The physical and chemical properties of four produced water samples from the AL-Hamada oilfield in the Libyan Arab desert were characterized. Produced water contains numerous potential factors that contribute to its aquatic toxicity. One of these is Total Dissolved Solids. TDS in high levels arises from the anions (chloride, sulfate and carbonate). The TDS was found to be close to the limits of TDS in produced water which is between 100 ppm to 300,000 ppm, in addition the COD was believed to be at a normal level where the high value of COD in produced water indicates numerous that it have numerous dissolved pollutants. There was not a big difference in alkalinity values in all samples as well as for hardness. Also there was no significant difference between the pH values for all samples and there was no correlation between pH and any particular parameter.

Overall, the physical properties of the produced water are considered to suggest a moderate effect on the environment.

Chapter 3

Inorganic compounds

3- Inorganic compounds in produced water

Produced water contains many inorganic materials (arising from source minerals from the geological formations (Strømgren *et al.* 1995). These include salts as described in detail in Chapter 2, certain heavy metals and other chemicals (Li *et al* .2006). Inorganic compounds present in produced water can be of two types either insoluble (inorganic colloids, grit, precipitates or scale which will be described in chapter **(5)** on oilfield chemicals or soluble, i.e., the salt content (salinity) (Hayes and Arthur 2004). Anions of inorganic salts include chloride, sulfate, carbonate and bicarbonate. Cations include sodium and potassium, iron, calcium and magnesium. Non-charged inorganic include silicate (H_4SiO_4) and borate (H_3BO_3) (Hayes and Arthur 2004). The diagram below shows the constituents of inorganics in produced water in both phases insoluble and soluble (Hayes and Arthur 2004).

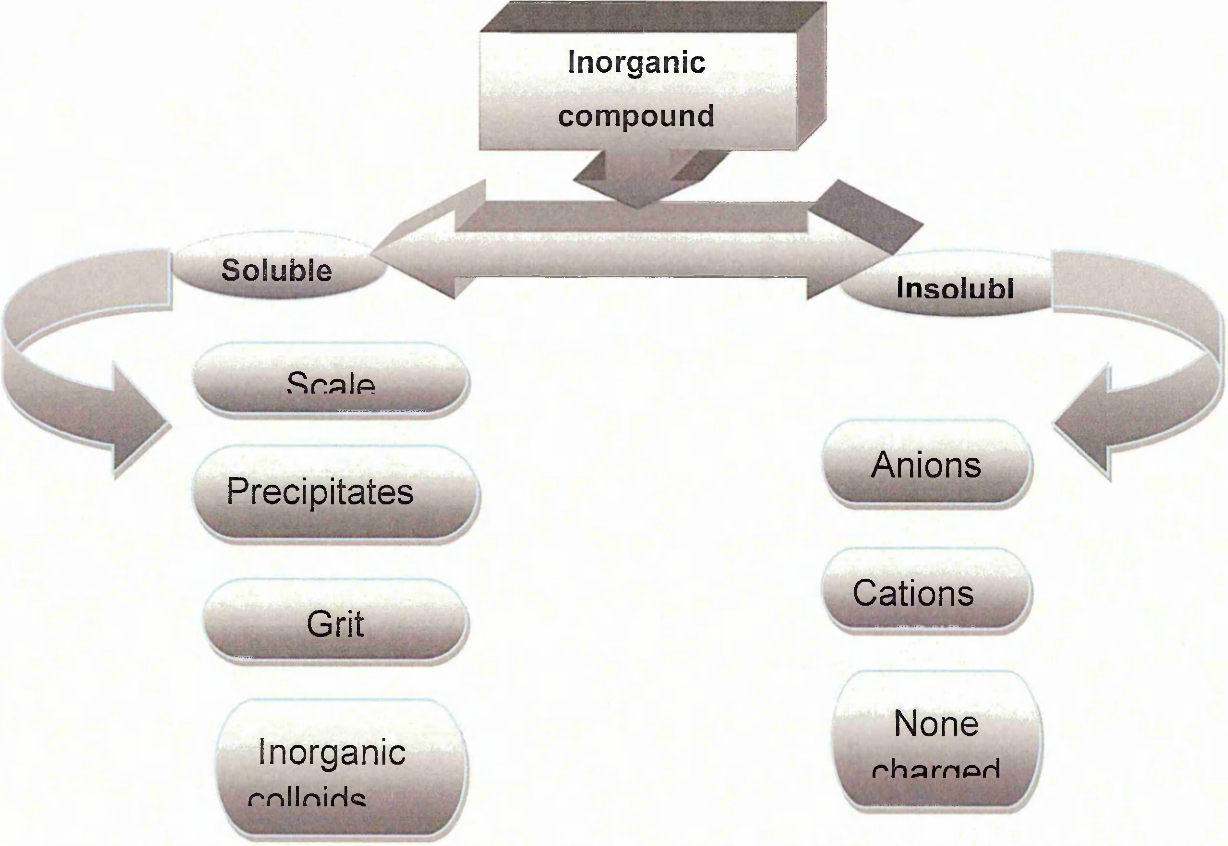

Figure 3.1 Inorganics in produced water in insoluble and soluble phases

3.1 Heavy metals in produced water

The main heavy metals that are present in produced water are manganese (Mn) ,vanadium (V) , nickel (Ni) , zinc (Zn), copper (Cu) , chromium (Cr) , cadmium (Cd), mercury (Hg) lead (Pb), boron (B), iron (as oxyhydroxides of iron), strontium (S), barium (Ba) (as scale as barium sulfate) and radium (Ra) (which may precipitate with sulfate, Neff 1987). Some metals have not been found such as aluminum (Al) and arsenic (As) **(**Rabalais *et al.* 1991). Moreover the sources of the mercury found could be other than produced water. (Offshore Produced Water Waste Management, 2001**).**

Ions in seawater possibly react with several of the heavy metal ions in produced water to establish insoluble precipitates (Stephenson *et al.* 1994). For example, barium is one of these ions and it is found in produced water discharges in the Gulf of Mexico (Trefry *et al.* 1996).

Apart from barium and zinc, metals in the northern GOM were within one to two orders of magnitude of the equilibrium sea water values (Offshore Produced Water Waste Management, 2001**).** Barium with radium precipitates as sulfate if seawater (high in sulfate) is used for water –flooding. Thus, In spite of the increase in the volume of the produced water with the age of the well, total mass loadings of metals discharged in produced water may not increase. In some cases mass loadings of some metals may actually decrease (Neff 2002).

Most metals from produced water do not have a noticeable effect on the environment and do not threaten marine organisms (Offshore Produced Water Waste Management, 2001**).** This can be explained by the reduction in concentration by dilution and since the form of the metals adsorbed onto sediments is less bioavailable to marine animals than metal ions in solution (Stephenson 1992). But if metal concentrations are sufficiently high, chronic toxic effects can be caused to exposed marine organisms and also metals can cause production problems. For instance, oxygen in the air can react with iron in produced water to produce solids, which can interfere with processing equipment, such as hydrocyclones, and can plug formations during injection or cause staining or deposits at onshore discharge sites (Veil *et al.* 2004).

3.2 Concentration of metals in produced water

The concentration of metals in produced water depends on the age and geology of the formation from which the oil and gas are produced (Veil *et al.* 2004). The concentrations of different metals in produced water discharged by Shell Expro and NAM in to North Sea are regularly up to about 1000x higher than the levels of injected seawater (Jacobs *et al.*1993). Significantly higher concentrations of cations were found in produced water from gas / condensed platforms than those occurring naturally in seawater, but the pattern of concentration of metal in effluents from oil platforms closely resembled the composition of (far offshore) North Sea seawater (Jacobs *et al.* 1993). If produced water is discharged to the open ocean, the concentrations will be rapidly diluted below the 1% level in minutes. But the dilution by insoluble precipitates with anions in seawater will reduce metal ion concentrations at a faster rate than by dilution alone. These dilutions prevent metals or hydrocarbons in produced water causing toxic effects in marine organisms except for organisms living on the platform near the discharge pipe (Offshore Produced Water Waste Management, 2001).

Arsenic has been found to occur at high concentrations in several species of marine animals at reference and discharge sites.

Barium also may be present at high concentrations of sulfate. It is considered to be 3 times higher than that of seawater, it is concentrations ranging from <0.1 to 2,000 ppm, depending primarily on the sulfate ion concentration (Neff and Sauer, 1995).

The metals V, Ni Zn, Cu and Cr are present at high concentrations in most discharges (Rabalais *et al.* 1991). The metals barium, copper, iron, mercury, and nickel were present in ambient seawater 2000 m from one or more discharge sites at higher concentrations (approximately two-fold) than in seawater at reference sites (Offshore Produced Water Waste Management, 2001). In spite of this, the concentrations of copper, iron, manganese, zinc, cadmium, chromium, lead, mercury were within their expected natural ranges (Offshore Produced Water Waste Management, 2001).

Simultaneously alkaline (Li, Na, and K) and alkaline-earth (Mg, Ca, Sr and Ba) metals indicated the highest concentrations in all cases; in particular the calcium concentration was higher than magnesium (Jacobs *et al.* 1993).

Table 3.1 Background level of some metals in produced water in the North Sea

Metal	**Concentration** (µg/l)	**Reference**
Barium	<50 - 80 22	(Tibbetts *et al.* 1992) (Brewer 1975)
Lead	20-100	(NSTF 1993)
Cadmium	4- 28	(NSTF 1993)
Iron	1.8	(Brewer 1975)
Copper	20-410 0.5	(NSTF 1993) (Brewer 1975)
Mercury	0.03	(Brewer 1975)
Nickel	<2-10 1.5	(Tibbetts *et al.*1992) (Brewer 1975)
Zinc	< 5 823	(Tibbetts *et al.* 1992) (Brewer 1975)

3.3 Techniques used to determine metals in produced water

Many techniques have been used to analyze inorganic constituents in produced water, such as, ion-selective electrodes and inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Hayes and Arthur 2004). Individual metals must be determined using methods demonstrating the total content of each metal, down to its background level in the seawater. In fact the detection limits for one method have been established on data for the background levels of metals in the North Sea (Olf 2003). However diverse heavy metals in produced water have been studied by both industry and government. The metals commonly studied are barium, cadmium, chromium, copper, lead, nickel silver and zinc (Ooc 1975; Jackson 1979; lysyj 1981; Ooc 1982; Burns 1983; Neff 1988; Neff *et al* .1988; SAIC 1991).

The metal contents reported are often dominated by the presence of barium and iron (Røe Utvik 1999).

Table 3.2 Requirements for qualification limits and methods used to determine metals in produced water (Olf 2003).

Metal	Requirement qualification limit (µg/l)	Possible methods
Chromium	1.5	AAS / ICP-MS / DRC-ICP-MS/ HR-ICP-MS
Nickel	9	AAS / ICP- MS / DRC-ICP-MS / HR-ICP-MS
Copper	6	AAS / ICP- MS / DRC-ICP-MS / HR-ICP-MS
Zinc	15	AAS / ICP- MS / DRC-ICP-MS / HR-ICP-MS
Cadmium	6	AAS / ICP- MS / DRC-ICP-MS / HR-ICP-MS
Lead	1.5	AAS / ICP- MS / DRC-ICP-MS / HR-ICP-MS
Mercury	0.1	CV-AAS/Au-amalgamation
Arsenic	1	HG-AAS / ICP-MS / DRC-ICP-MS
Barium	10	AAS / ICP- MS / DRC-ICP-MS / ICP-AES
Iron	1	AAS / ICP- MS / DRC-ICP-MS / ICP-AES

3.4 Materials and methods:

3.4.1 Instrument and method used

ASTM D 1971 standard method was used to determine the heavy metals content in collected samples. The concentration of 13 metals (Aluminum, Silver, arsenic, barium, cadmium, chromium, copper, Iron, mercury, manganese, nickel, lead, and zinc) were then analyzed by using Inductively Coupled Plasma- Optical Emission Spectrometer (ICP-OES), (SPECTRO Analytical Instruments, Model: Vista-PRO Simultaneous ICP-OES ,Varian, Australia) .The instrument includes a CCD array detector with the ability to capture the entire wavelength spectrum in one reading without scanning. Vista-MPX captures the entire spectral image in one reading, interferences are easily avoided by choosing any wavelength from 175-785 nm. simultaneous background correction and internal standardization–resulted in more accurate and precise results with excellent long term stability. The unique MPX CCD array detector is cooled to -30°C for the ultimate in low noise performance and best possible detection limits. Superior plasma performance from over 75% RF coupling efficiency the flexibility and easily analyze to full range of sample types.

The instrument was calibrated for the measurement of emission by standard solutions and a blank with multiple element standard solutions (0.05, 0. 2, 0.5,1 ppm) to cover the wide range of metal concentrations, aluminum(Al) , silver(Ag), arsenic(As), barium (Ba), cadmium (Cd), chromium(Cr), copper(Cu), Iron(Fe), mercury(Hg), manganese(Mn), nickel(Ni), lead(Pb), and zinc (Zn) standard solutions were prepared fresh from individual element stock standard solutions (1000 $\mu g\ ml^{-1}$), were (TraceCERT^{TM} Ultra) supplied by Fluka.

Table 3.3 Conditions used in (ICP-OES) instrument

Power (kW)	1.2
Plasma Flow (l/min)	15.0
Auxiliary Flow (l/min)	1.50
Nebulizer Flow (l/min)	0.75
Viewing height (mm)	10
Replicate read time (s)	3
Instrument stabilization delay (s)	15
Sample uptake delay (s)	30
Pump Rate (rpm)	15
Rinse time (s)	15
Replicates	3

3.4.2 Procedure

All glassware was soaked in 25 % v/v nitric acid prior to use for several days ,rinsed with hot nitric acid and then rinsed several times with de-ionized water.

100 ml from a well mixed, acid preserved sample (5 ml of sp gr. 1.42 concentrated HNO_3 per litre of sample) was transferred to a 150-mL beaker , and 5 ml of HCl (sp gr 1.19) was added. Then the beaker was placed on the hot plate in a fume hood for solution evaporation. The volume of the sample aliquot was reduced to about 20 ml by gentle heating for about two hours. After beaker had cooled the sample solution was transferred quantitatively to a 100-ml volumetric flask, diluted to volume with reagent water, stoppered and finally mixed for direct analysis by ICP-OES. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

3.5 Results & Discussion

3.5.1 Results

A number of heavy metals have been determined in the samples collected; the results are reported in Table 3.4 and Figure 3.2. These show the concentration of the elements Ba, Fe, Mn, Pb, and Zn in all samples. For comparison Table 3.5 presents data for heavy metals in the North Sea and sea water (Tibbetts *et al.* 1992).

Table 3.4 Concentration of heavy metals in samples collected (mg/l)

Sample No	S1	S2	S3	S4
Al	< 0.01	< 0.01	< 0.01	< 0.01
Ag	< 0.01	< 0.01	< 0.01	< 0.01
As	< 0.02	< 0.02	< 0.02	< 0.02
Ba	0.36	0.58	0.38	0.07
Cd	< 0.02	< 0.02	< 0.02	< 0.02
Cr	< 0.01	< 0.01	< 0.01	< 0.01
Cu	< 0.03	< 0.03	< 0.03	< 0.03
Fe	< 0.03	0.225	0.02	< 0.03
Hg	< 0.02	< 0.02	< 0.02	< 0.02
Mn	0.06	0.23	0.07	0.2
Ni	< 0.03	< 0.03	< 0.03	< 0.03
Pb	0.043	0.07	0.043	<0.04
Zn	0.203	< 0.01	< 0.01	0.04

Values in the table are related to the limit of detection of the instrument used which detects each element separately.

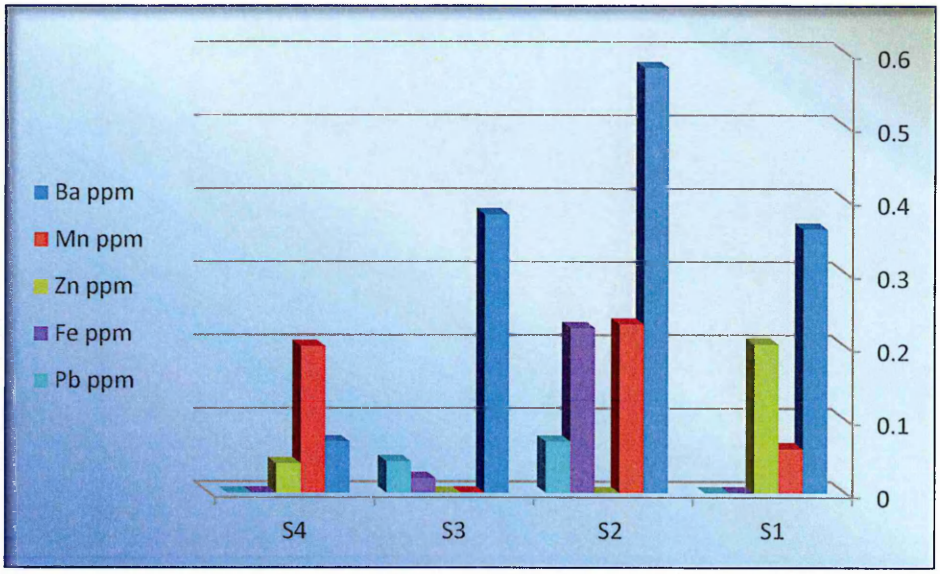

Figure 3.2 Concentrations of heavy metals in the samples collected

Table 3.5 Concentration of heavy metals in produced waters in the North Sea and sea water (mg/l) (Tibbetts *et al.* 1992).

Metal	North Sea	Sea water
Iron	1-33	< 0.02-0.5
Aluminium	None quoted	0.04-0.18
Barium	1.3- 218	0.05.0.08
Cadmium	None quoted	< 0.005-0.1
Chromium	None quoted	< 0.02
Copper	0.01- 1.0	0.01- 0.03
Manganese	None quoted	< 0.002-0.01
Nickel	None quoted	< 0.02-0.01
Lead	3.3 – 8.8	<0.03
Zinc	0.01-35	< 0.005
Arsenic	None quoted	< 0.01
Mercury	None quoted	0.05
Silver	None quoted	< 0.01

3.5.2 Discussion:

Heavy metals content

According to the experimental results, Table 3.4, all samples showed either very low concentrations (e.g. less than the detection limits) for the metals, aluminum, silver, arsenic, cadmium, chromium, copper, mercury, and nickel, and some cases for zinc, or low detected concentrations for the metals iron, lead, manganese.The only metal present in high concentrations was barium, this was probably a consequence of precipitation of barium sulfate scale.

Barium concentrations have been reported to range from <0.1 to 2,000 ppm in produced waters, depending primarily on the sulfate ion concentration (Neff and Sauer, 1995). All samples from the Al-Hamada field contained detectable quantities of barium. It is significantly higher than the other metals analysed ranging from 0.07 to 0.58 ppm.

Manganese was detected in all samples except sample 3 which was below the detection limits. The levels found were higher than those reported for sea water and North Sea water.

The ranges of concentrations of metals detected in all samples are close to the composition of seawater but less than the North Sea (compare data in Tables 3.4 and 3.5).

3.6 Conclusion

Metals typically found in all samples include barium, iron, manganese,lead, and zinc, while the metals aluminum ,silver, arsenic, cadmium, chromium, copper, mercury, and nickel were not detected in any of the samples collected..

The highest value for metal was reached for barium and it is precipitated at elevated level concentrations compared to other metals in all samples. This was possibly a consequence of precipitation of barium sulfate scale. Over time, the metal concentrations in produced water often change regularly to be like the metal concentrations in modern seawater (Stephenson *et al.*, 1994) due to this fact the sample no 4 (Pit) showed similar patterns of concentration for the metals Ba, Mn, Zn reversed compared to seawater.

The results indicate that none of the metals is likely to be present at high concentration in all samples; higher levels of metals may exist in sediment.

Heavy metals generally cause little or no effects in marine organisms if discharged to the open ocean because of the rapid dilution.

On the whole, heavy metal content in samples was moderate and within the expected natural ranges, as quoted in the literature, except for manganese.

Chapter 4

Organic compounds in produced water

4- Organic compounds in produced water

4.1 Classes of compounds present, amount and simple techniques for estimating the amount of organic compounds present in a water sample.

4.1.1 Classes of organic compounds in produced water

Produced water can contain both hydrocarbons and non-hydrocarbons. Hydrocarbons are defined as organic compounds composed of carbon and hydrogen only. Non-hydrocarbons can contain carbon, hydrogen oxygen, nitrogen and sulfur (Brown *et al.* 1992). Hydrocarbon can become dissolved in produced water due to its nature and its expression by the oil phase (Morrow *et al.* 1995). During the production process, the oil droplets and components from the oil and the added production chemicals will disperse or dissolve into the production water; therefore organic constituents can exist in produced water as either dispersed oil droplets or as dissolved organic compounds (Colin *et al.* 2005).

The most common organic contaminants found in coproduced water are (Veil *et al.* 2004; Benko and Drewes 2008).

- Oil and grease which can be found in three forms:
    - Free oil (this is in the form of large droplets),
    - Dispersed oil (this is in the form of small droplets),
    - Dissolved oil (these are hydrocarbons and other similar materials that are dissolved in the water stream).
- Organic acids, dialiphatic fatty acids (carboxylic acids) and the aromatic acids.
- Aromatic hydrocarbons, monocyclic aromatics (ethylbenzene, benzene and toluene) and polycyclic aromatics (PAH).

- Polar compounds, e.g. phenols. In addition "polars" include a number of dissolved compounds, typically organic acids (Offshore Produced Water Waste Management 2001), which contribute to the high chemical oxygen demand (COD) in the water and it is difficult to treat for the petroleum industry (Li *et al.* 2006).

4.1.2 Concentration levels and simple techniques for estimating the amount of organic compounds present in a water sample.

A number of tests are used to give a measure of the total amount of organic compounds present in water samples.

The hydrocarbon fraction of the organics in produced water is relatively unreactive, however some of the treatment chemicals are. Chemical Oxygen Demand **(COD)** is a significant parameter used for the evaluation of the concentration of organic contaminants in water (Li and Song 2009), since the degradation of organic compounds generally requires oxygen. However the presence of high concentrations of acetic acid can lead to an underestimation of the total organic when COD is used. Since a large part of the organic portion of produced water consists of low molecular weight carboxylic acids (acetic-valeric) this is an issue in this work. Another parameter used to give a measure of contamination is Total Organic Carbon **(TOC)** (typically measured by combustion). This is made up from all of the combustible material ie. organic acids, phenols and hydrocarbons. TOC ranged from 220,000 ug/l to 298,000 ug/l in produced waters from Eugene Island and Lake Pelto (Offshore Produced Water Waste Management 2001).Total hydrocarbons **(TH)** is determined by either infrared spectroscopy or gas chromatography, in the same samples this ranged from 30,900 ug/l to 20,400 ug/l. The term “total petroleum hydrocarbons” (TPH) is generally used to describe the measurable amount of petroleum-based hydrocarbons in the environment. The TPH information obtained also depends on the analytical method used, for example, in one gas chromatographic method the TPH value is derived from the total concentration of C5-C36 n-alkanes. The regulatory limit for total petroleum hydrocarbons **(TPH)** in produced waters discharged offshore in the North Sea is 40 mg/l (Durell *et al.* 2006).

4.2 Soluble organic compounds in produced water

Polar functional groups can make organics soluble in produced water. Soluble compounds range from low molecular weight (C2-C5) carboxylic acids and naphthenic acids (Morrow *et al.*1995), to acetone, and methanol, ketones, and alcohols, which contain polar groups, to higher molecular weight hydrocarbons (C6 to C15), (which are also soluble in water at low concentrations (Veil *et al.* 2004). The category of oil that can be found in produced water is called "soluble oil". Benzene and polycyclic aromatic hydrocarbons (PAH) also have a slight solubility in water (Morrow *et al.* 1995), along with certain treatment chemicals (Colin *et al.* 2005).

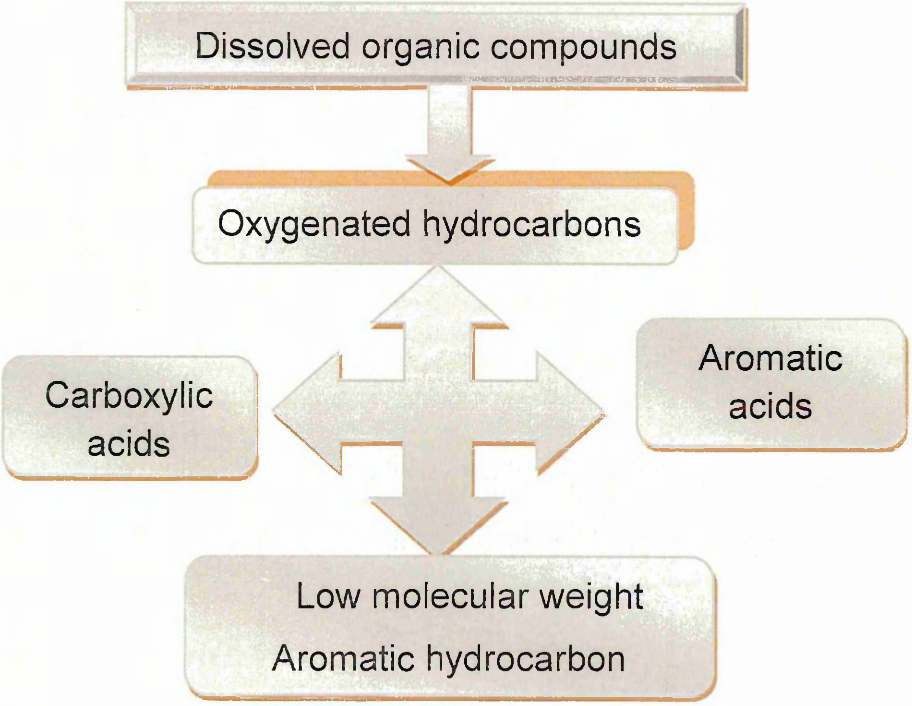

Figure 4.1 Form of the dissolved organic compounds

The chemistry of soluble organics and their impact on total effluent toxicity is not understood. They are difficult to treat, and represent significant treatment problems for the petroleum industry (Bostick *et al.* 2002). The concentration of dissolved organic components in some produced water has been found to exceed the permissible levels of organic contaminants in the water (Thoma *et al.*1999). As an illustration in some produced water, the concentration of these components is greater than 5,000 ppm (Veil *et al.* 2004; Bostick *et al.* 2002). However pH has a large effect on organic solubility and also temperature, from data on these variables studied in the laboratory (Mcfarlane *et al.* 2002). In fact the amount of dissolved hydrocarbons in produced water and refinery effluents is increased by polar constituents of deep-water crude (Bostick *et al.* 2002), and it is dominated by the volatile aromatic fraction of the oil, namely benzene, toluene, ethyl benzene and xylene (BTEX) (Toril 1999). A number of studies have focused specifically on the acid fraction of soluble oil in produced water, which is important for sea water samples (Stephenson 1992). However the major portion of the soluble oil in produced water sometimes can be the aromatic carboxylates (Colin *et al.* 2005). Gravimetric and infrared spectroscopy methods have been utilized to measure soluble organics in brines (Mcfarlane *et al.* 2002).

4.3 Dispersed and dissolved oil in organic material in produced water

As has been said earlier "oil" is the general term used for mixtures of organic material such as aromatics, aliphatic, organic acids, phenols and a variety of other materials (Thoma *et al.* 1999), which are dispersed or dissolved in produced water at the time of discharge (Stephenson 1992).

The content of the oil phase in produced water can in fact be expressed as follows (Yang 2006):

Dissolved oil, which is water soluble fraction of oil in water, it consists of

- Aromatics (BTEX, PAH and naphthenic acids)
- Short chain carboxylic acids (Formic acid, glacial acetic acid, propionic acid, butyric acid, valeric acid)
- Phenols

Dispersed oil which describes oil in produced water in the form of small droplets, which may range in size from sub-microns to hundreds of microns and contains

- Aromatics mainly PAH
- Acids (fatty acids, naphthenic acids)
- Aliphatics

The amount of dispersed oil in a produced water sample depends on several factors (Veil *et al.* 2004).

- Density of oil
- Shear history of the droplet
- Amount of oil precipitation
- Interfacial tension between the water and the oil

The total oil content (dispersed + dissolved) can range from 40 mg/l to 2,000 mg/l (Ali *et al.* 1999). This was measured in accordance with the existing standard, which as of 1 January 2003 is ISO NS-EN 9377-2.

Whilst other methods could also be used, for instance, on-line analysis (Olf 2003), small quantities of free oil as small oil droplets dispersed in the water, when present in low quantities of 1 ppm cannot be detected accurately by the current commercial instruments. There are in fact no reports in the literature of a direct method to measure dispersed oil in water (Morrow *et al.* 1995). The standard methods that are used are based primarily on solvent extraction followed by an infrared (IR) quantification step (e.g. EPA methods 413.1 and 413.2 (Morrow *et al.* 1995). Using these methods the main components measured are the volatile aromatic hydrocarbons, particularly benzene, toluene, ethylbenzenes and xylenes (BTEX), which are the poorly water soluble hydrocarbons components of the oil (Boylan and Tripp, 1971). When produced water samples are taken and acidified more water soluble organic acids and phenols are converted from being water soluble (dissolved) to oil soluble (dispersed). Treatment of the extract using florisil usually removes them out, and hence these are not included as oil in the infrared measurement if this step is taken in the analysis method (Yang 2006). In contrast, a direct logging technique that has been used for detecting oil and drill cuttings for decades is based on a fluorescence method. The method is quantifying the amount of hydrocarbons including crude oil dispersed in water at low levels by comparing the emission fluorescence of the mixture (surfactant and water) to previous correlations which are drawn between known amounts of hydrocarbon in water and their emission fluorescence under similar conditions. For example three processes developed recently employ fluorescent measurement to test for the presence of hydrocarbons within drill cuttings. One process appropriate only to oil base mud drill cuttings is disclosed in U. S. Patent No. 4,609,821 (Morrow *et al.* 1995).

Free oil in fact with the byproduct of oil represents only about 2% to 12% of the actual fluids lifted to the surface, oil wells in the U.S. viewed as “dirty water wells”(Godshall 2006).

4.3.1 Aliphatic and aromatic compounds

4.3.1.1 Aliphatic and aromatic composition

Aliphatic hydrocarbons include alkanes, alkenes, and alkynes (Yang 2006), on the other hand aromatic hydrocarbons are substances consisting of carbon and hydrogen that contain a benzene ring in their molecular structure (Veil *et al.* 2004). Whereas Monocyclic aromatic hydrocarbons (contain one aromatic ring) i.e. BETX (benzene, ethyl-benzene, toluene, and xylene) (Veil *et al.* 2004;Yang 2006; Neff 2006), polycyclic aromatic hydrocarbons (PAH) are hydrocarbon molecules with several aromatic rings (Veil *et al.* 2004; Yang 2006). In oil the most abundant 4–6 ring PAH are C1 fluoranthenes and pyrenes and C1- and C2-chrysenes), NPD naphthenic (naphthalenes ,C1naphthalene, C2naphthalene, C3naphthalene phenanthrenes, anthracene, C1phenanthrene, C2phenanthrene, C3phenanthrene along with sulfur containing compounds dibenzothiophenes, C1dibenzothiophene, C2dibenzothiophene, C3dibenzothiophene) (Olf 2003; Guidance notes for the sampling and analysis of produced water and other hydrocarbon discharges). Since the composition of PAH is so complex the U.S. EPA has identified the 16 priority PAH that should be measured to give an indicative measure of total concentration of PAH (Hawboldt and Adams 2005).

Table 4.1 The 16 PAH identified by U.S. EPA for measurements.

Compound	Molecular Mass g /mol
naphthalene	128
Acenaphthylene	152
Acenaphthene	154
Fluorene	166
Phenathrene	178
Anthracene	178
Fluoranthene	202
Pyrene	202
Benzo(a)anthracene	228
Chrysene	228
Benzo(b)fluoranthene	252
Benzo(a)pyrene	252
Indeno(1,2,3-cd)pyrene	276
Dibenzo(a,h)anthracene	278
Benzo(ghi)perylene	276
Anthantherne	276

naphthalene is the most simple PAH, and it is normally present in higher concentrations than other PAHs, which range from relatively "light" to "heavy" soluble. The less soluble PAHs in water are associated with dispersed oil and are those of higher molecular weight (Veil *et al.* 2004).

4.3.1.2 Concentration of aliphatic and aromatic compounds in produced water

Dissolved aliphatic hydrocarbons concentrations in produced water ranging from 606 to 2. 7 mg/l have been determined in paraffinic oils (Ooc, 1975;

lysyj 1981, Ooc, 1982; Burns and Roe Industrial Services 1983; Middleditch1983; Caudle and Stephenson 1988; Brown *et al.* 1990).

Monocyclic aromatic hydrocarbon concentrations in produced water from oil platform samples (where dilution from 50- to more than100-fold occurs within 5 m of the discharge) ranged from 1,754 to 5,183 µg/l (Offshore Produced Water Waste Management 2001). In one study of Produced Water the 16 EPA PAHs concentration ranged from 0.7 to 100s mg/l (Hawboldt and Adams 2005). PAH concentrations ranged from 58 to 596 ug/l in produced water from oil platforms in the (GOM) (Texas and Louisiana) (Offshore Produced Water Waste Management 2001). The major components identified were the low molecular weight naphthalenes, fluorenes, and phenanthrenes, and their concentrations were much higher than normally found in seawater. In contrast, six ring PAHs (high molecular weight) were present at concentrations <0.1 ug/l or below the detection limit (Offshore Produced Water Waste Management 2001).

As an illustration Table **4.2** shows the concentrations of PAH in Produced Water from Norwegian, UK and Dutch Oil fields (Hawboldt and Adams 2005).

Table 4.2 PAH in produced water from Norwegian, UK and Dutch oil fields (mg/l)

Compound	Norwegian Oil	UK Oil	Dutch Oil
NPD	0.8-10.8	0.007-0.7	4 0.22-0.4
PAH - EPA 16 except N and P	0.001-0.13	0.002-0.12	0.12-0.285

4.3.1.2 Volatiles and semi volatiles aromatic compounds

Volatiles, in particular BTEX, in produced water are considered to be highly soluble (Rabalais et *al.* 1991). They are also acutely toxic to organisms exposed to high concentrations (National Research Council 1985, Boesch and Rabalais 1987). The U.S.-EPA specified: three volatile organic compounds (benzene, toluene and ethylbenzene) four semi-volatile organic compounds (SVOCs) phenol, fluorene, benzo (a) pyrene (BAP), and bis (2-ethylhexyl) phthalate (BEHP) (Offshore Produced Water Waste Management 2001), to be measured as representative of the whole.

Volatile hydrocarbons in produced water can also occur naturally (Veil *et al.* 2004), at significantly high concentrations (Lu *et al.* 2006), up to 481 mg/l. Of these 75% to 95% are benzene and toluene with benzene making up 50-88% of the total (Jacobs *et al.* 1993).

The concentrations of volatiles measured in produced water from gas platforms are higher than from oil platforms (Offshore Produced Water Waste Management 2001).

BTEX and other volatile compounds in water have been determined by utilizing gas chromatography-flame ionization detection (GC–FID) or gas chromatography–mass spectrometry (GC–MS) with a quantification limit of 1.0 µg/l. In order to avoid evaporation of BTEX during sample processing, headspace or purge-and-trap techniques must be used (Olf 2003). Headspace solid-phase (SPME) extraction has also been used (JI *et al.* 2006). Standard U.S.-EPA Method (8270C) protocol has been used to analyse semi-volatile organic compounds (Bostick *et al.* 2002). Packed tower aeration (PTA) or air stripping was used to remove volatile organic compounds (Hackney and Wiesner 1996). Produced water composition is different from field to field, so each field should be assessed with respect to which compounds contribute to the environmental risk.

4.3.2 Acids

The organic acid fraction of oil can be in two type - aliphatic fatty acids (carboxylic acids: formic, acetic, propionic, butyric and valeric acid) and the aromatic acids (naphthenic acid) (Rabelais *et al.* 1991). The detailed chemical characterisation of naphthenic acids is not in fact known (Stephenson 1992).

Fatty acids occur naturally in sea water, and are found in produced water as sodium salts of the acids (Somerville, 1987). High concentrations of simple fatty acids are found in produced water arising from paraffinic oils, while noteworthy amount of naphthenic acids are found in produced water arising from the presence of asphaltenic oils (Stephenson 1992).

Organic acids are integrated into the oil during source rock maturation (e.g. Mackenzie *et al.*, 1983). Acetic and valeric acids comprise the large fraction of the organic portion (Meredith *et al.* 2000).

Either the formation of acids during biodegradation, or the preferential removal of non-acidic compounds, lead to a relative increase in the concentration of the acidic components (Behar and Albrecht, 1984).

SImple organic acids (i.e. formic, acetic, and propionic acids) have been measured in produced water at a total concentration of 30mg/l (Bostick *et al.* 2002) and 50 mg l^{-1} (Mcfarlane *et al.* 2002). The major organic acid found in produced water in studies is acetic acid making up 70 to 94% of the total in Shell Epro and NAM platforms (Jacobs *et al.*1993), and is also present at 700 mg/l in North Sea Produced Water (Somerville, 1987). Organic acids can be determined by direct GLC/FID (Tibbetts *et al.* 1992), GC-MS, ionic chromatography, and isotachophoresis (ITP) (Brendehaug *et al.* 1992). The quantification limit is 2 mg/l (Olf 2003).

4.3.3 Phenols

Phenols in water arise with all three types of oils and also from gas condensate operations (Callaghan and Baumgartner, 1990). The phenols found in produced water are generally alkyl phenols up to C7 (Røe Utvik 1999). Large numbers of alkyl phenols are found in an average sample of produced water, but thiophenols and naphthol compounds have not been widely studied. Only alkyl phenols and naphthols are quantified generally since the GC techniques used cannot achieve the desired degree of separation of thiophenols (Boitsov *et al.* 2007). The level of phenolic compounds in produced water depends on the type of production gas or oil (Brown *et al.* 1990). For instance produced water from gas operations tends to have high quantities of phenols (Stephenson 1992). Phenolic compounds in produced water, principally alkylated phenols, are toxic towards bacteria or higher marine organisms (Frost *et al.* 1998), as a result of their high concentration and highly solubility. (National Research Council 1985, Boesch and Rabalais 1987).Phenols and alkyl phenols in produced water are however readily degraded by bacterial and photo-oxidative processes in both seawater and marine sediments (Brown *et al.* 1990).

Phenols and C1-C9 alkyl phenols in produced water are typically determined by GC-MS with 0.1 µg/l quantification limit (Olf 2003).

4.4 Materials and methods:

4.4.1 Instruments and methods used

4.4.1.1 Total petroleum hydrocarbon and total oil and grease (TPH/TOG)

Total oil and grease and total Petroleum Hydrocarbon were determined by I.R. (TPH-IR) according to (U.S-EPA Method 413.2 & 418.1 using solvent S-316) by means of an Infracal TOG/TPH analyzer, model CVH from Wilks Enterprise, Inc. A dual detector is used in the TOG/TPH Analyzer to measure hydrocarbon concentrations at 3.4 micrometers (2940 cm^{-1}) with a reference at 2.5 micrometers (4000 cm^{-1}). A standard 12 volt power supply is provided with the analyzer, and this may be operated from any grounded a.c. outlet (line power requirements: 100 – 250 VAC, 50-60 Hz, 0.5-0.3 amps).

The instrument was allowed to warm up for 1 hour prior to use and the analyzer calibrated with sets of mixed oil and solvent volumetrically standards prepared in the working range of 0 to 1000 mg/l in (S 316) using B-heavy oil (Nacalai tesouse.inc Kyoto Japan).

4.4.1.2 Base/ Neutrals Acids

Base / Neutrals were determined according to the Standard Method U.S.-EPA 625 and then were analyzed by GC–MS, Hewlett-Packard Avondale ,PA,USA HP5890 Series ii gas chromatograph with HP 5971 MS mass selective detection. Three standard solutions (2 : 10, 40: 10, 100: 10 ng/ml) were prepared from 2000 µg/ml of EPA phenols mixture in methanol supplied by Supelco, Bellefonte, PA using internal standard chrysene–d_{12} to identify the acid fraction and (2:10 ng/ml, 20:10 ng/ml, 40:10 ng/ml, 100:100 ng/ml) standard solutions were prepared from 200 ng/l of mixed EPA 625 Base-Neutral 1,2,3 and 4 stock solutions in dichloromethane supplied by

Supelco, Bellefonte, PA with internal standard chrysene –d12 to identify the Base-Neutral fraction.

Table 4.3 Chromatographic conditions used for Base / Neutrals acids

Instrument name	HP 5890 Series II (GC–MS)
Injector temperature	275 ° C
Column:	28.0 m, 0.25 mm I.D. 0.25 µm film thickness
Column temperature	50 °C(hold 4 min) to 250 °C @ 6 °C/min, which was followed by a second rate of 20 °C/min to a final temperature of 300 °C.
Detector temperature	300 °C
Carrier Gas	Helium

4.4.1.3 Volatile organic compounds (BTEX)

Volatile organic compounds (BTEX) analyses were carried out by solid-phase microextraction (SPME) following ASTM standard methods D 6520

GC analyses were performed using a Varian 3800 gas chromatograph with Varian CP 8400 auto-sampler and coupled to a flame ionization detector (GC-FID).

Table 4.4 Chromatographic conditions used for BTEX

Instrument name	Varian GC CP 3800
Injector temperature	280 °C
Column:	CP-5 (30m x 0.32 mm ID with a film thickness of 0.25 µm
Column temperature	Programmable at 40 °C for 2 minutes ,ramped to 12 °C /min and then held at 300 °C for 10 min
Detector temperature	300 °C.
Carrier Gas	Helium

SPME holder and fibers

SPME holder and fiber assemblies for manual sampling were provided from Supelco (Bellefonte, PA, USA).

Table 4.5 Headspace SPME parameters

Fiber coatings used	100µm polydimethylsiloxane (PDMS) red /plain
Extraction time	10 min
Stirring rate	200 rpm
Ratio of head space	3.0 ml of headspace (1.0 ml water sample in 4.0 ml vial)
Sodium chloride concentration	0.1 g NaCl per 1 mL of sample

Standard solutions of BTEX at the concentration (50,100, 200, 400 ng l^{-1}) were prepared from 2000 ng l^{-1}stock solution purchased from Supelco (Bellefonte, PA, USA).

4.4.1.4 Polycyclic aromatic hydrocarbons (PAH)

The content of the polycyclic aromatic pollutants from the Environmental Protection Agency (EPA) priority list were determined by GC/MS-SIM using standards test method (EPA 610).

Table 4.6 Chromatographic conditions used for PAH

Instrument name	Gas Chromatography/Mass Spectrometry (GC/MS) techniques model a Hewlett-Packard 5890 series II, equipped with a Hewlett-Packard 6890 autosampler, Hewlett-Packard 5971A mass selective detector
Injector temperature	280 and 250°C
Column:	HP5-MS 30m×0.25mm I.D. 0.25µm film thickness
Column temperature	Temperature was initially held at 80°C for 3.5 min, ramped to 320°C at a rate of 10°C/min, and then temperature was held at 320°C for 7 min
Carrier Gas	Helium

The working standard solutions were prepared by diluting the 2000 µg/l stock solutions in acetonitrile at concentrations of 2 mg/l , 5 mg/l, 10 mg/l, 15 mg/l, 20mg/l). Certified standards of the 16 PAHs were purchased from Supelco (Bellefonte, PA, USA).

4.4.1.5 Semi-volatile organic compounds (phenols)

Total content of phenol was determined by photometer LF 2400 using reagent Cat.-No 37427 00 or N (refill) package 3746700 from Sigma–Aldrich Labortechnik .GMBH.

4.4.1.6 Carbon distribution of the oil extracted from the samples

The oil was extracted from the samples by liquid-liquid extracted with dichloromethane and the carbon distribution identified by GC analysis.

Table 4.7 Chromatographic conditions used for carbon distribution

Instrument name	GC with FID 3800 detector
Injector temperature	300 ^{O}C
Column:	CP-SISLS CB 60m
Flow Rate	1:2 ml/min split Ratio (1:20)
Column temperature	Programmable at 30 °C, ramped to 300 °C at rate 4 ^{O}C/ min for 20 min
Detector temperature	300 ^{O}C
Carrier Gas	Helium

4.4.2 Procedures

4.4.2.1 Total Petroleum Hydrocarbon (TPH)

140 ml of the sample was acidified with 4 M HCl to pH 2 or less with pH checked using pH indicating paper in a clean glass sample bottle. and then the sample transferred into, a separator funnel and 14 ml of solvent was poured into the empty glass sample and the bottle shaken to insure all of the oil and grease contents were extracted, the solvent (S 316) is added to the sample in the separator funnel and after two minutes of shaking, the solvent was allowed to separate, then the solvent was removed from the bottom of the separator funnel and passed through a filter cup with a hydrophobic, sreparatory phase filter paper disk. The filter cup was place into a clean glass funnel on top of the clean 25 ml glass graduated cylinder, the extraction was repeated twice with 14 ml of solvent. Extract of TOG was then placed in a l ml quartz cuvette that was placed into the sample holder of the instrument. the analysis displayed in mg/l. The solvent from the cuvette poured into a waste collection container. The cuvette was rinsed out with solvent and allowed to dry.

For TPH (total petroleum hydrocarbons) the samples were extracted the same way as TOG and then the extract was passed though silica gel to remove the polar organics and placed in the quartz cuvette.

4.4.2.2 Base / Neutrals acids

0.2 ml of surrogate standard spiking solution (2,2'-difluorobiphenyl . . ., decafluorobiphenyl, pentafluorophenol) 100 µg/ml in acetone were added to 200 ml of sample in the sample bottle and shaken. This was then transferred to 500 milliter separator funnels ,the pH of the aliquot checked with pH paper and adjusted to more than pH 11 by adding sodium hydroxide solution (10 N) and extracted with 60 ml of dichloromethane three times (20 ml each time).the extracts were combined and mixed well in Erlenmeyer flask, followed by drying over anhydrous Na_2S0_4, after which the volume of the extraction was reduced to approximately 2 ml by evaporation with a light of nitrogen gas flow, finally the extract was transferred to a screw cap vial and labeled as the base/neutral fraction.

The aqueous phase was adjusted to less than pH 2 by addition of 1:1 (v/v) sulfuric acid, and was then extracted the same way as the base/neutral fraction extracted above but here it was labelled as the acid fraction. The fractions were analyzed by GC/MS and as a means of checking the GC-MS instrument sensitivity and linearity the internal standards were added after solvent extraction.

The original sample was returned to a 500 ml graduated cylinder and the volume recorded.

4.4.2.3 Volatile organic compounds (BTEX)

The water samples were headspace extracted by a SPME technique

First 1 ml of the sample was saturated with NaCl, and agitated with a Teflon-coated stir bar. The SPME fiber was exposed over stirred samples and extracted, and then the fiber retracted into the needle of the holder; finally the extracts were desorbed, and analyzed with GC–FID.

4.4.2.4 Polycyclic aromatic hydrocarbons PAH

500 ml of the sample were extracted three times with the solvent dichloromethane (DCM) (30 ml each time) in a 1L separating funnel. The three extracted samples were mixed, then the volume was reduced to approximately 10 ml under gentle stream of nitrogen and filtered through 5

cm anhydrous sodium sulfate and the filters washed with DCM. The remaining solvent removed with a gentle stream of nitrogen to about 2 ml, finally the extract was transferred to a screw cap vial. The sample was then cleaned up to remove the aliphatic fraction. Dichloromethane was blown down to dryness under a gentle stream of nitrogen and 1ml cyclohexane was added.

The sample was eluted on a chromatographic column containing activated (130 °C overnight) silica (60-120 mesh BDH Ltd, Poole, England , particle size 0.13-.25 mm) in DCM and 1 ml of anhydrous sodium sulfate. The aliphatic fraction was eluted with pentane (20 ml) and discarded. An additional 1 ml of cyclohexane was added and the aromatic fraction was eluted with dichloromethane: pentane (4.75ml DCM:7.75ml pentane). Lastly the volume was reduced to 1 ml with a gentle stream of nitrogen and analysed by GC/MS.

4.4.2.5 Semi volatile organic compounds - phenols

To determine total phenol compounds, 10 ml of the sample was transferred into a reaction bottle, 2 drops of reagent 1 (diethanolamine and 4-amino -2,3 di methyl.1-phenyl- 3-pyrazolin- 5 one) were added and then the bottle was shaken for 30 s, after that 3 drops of reagent 2 (mixed reagent tests for photometer phenol) were added and the mixture was further shaken. The bottle was left for 2 minutes, followed by determination using a photometer LF 2400. This was done by switching on the Photometer and selecting the substance phenol. The instrument was zeroed with reagent water 5 ml and then 5 ml of the sample prepared in the reaction bottle was transferred to a clean cuvette and total phenol (mg/l) measured directly.

4.4.2.6 Carbon distribution of the oil extracted from the produced water samples

500 ml of the sample was extracted three times with 50 ml of DCM in a separator funnel. Extracts were combined and dried with 20g of anhydrous Na_2SO_4. The filtrate volume was reduced to 10ml. Prepared DCM extracts were then injected into a GC.

4.5 RESULTS and DISCUSSION

4.5.1Total petroleum hydrocarbon and total oil and grease (TPH/TOG)

The results of the concentrations of oil-and-grease and TPH components extracted from the produced water using U.S.- EPA Method 418.1 are given in Table 4.8 (refer to Appendix A for the table 4.9 and calibration graph of the instrument Figure 4.2).

Table 4.8 Concentrations of TOG and TPH in produced water samples from the Al-Hamada oilfield Libya

Sample No	TOG ppm	TPH ppm
S1	9.4	7.2
S2	4.2	2.1
S3	4	1.2
S4	1.6	1.2

An observation worth mentioning from the values in Table 4.7 is that the TOG concentration was slightly greater than TPH in all samples, but there were only minor variations in the concentration between them. This may be explained by the fact that the polar non-hydrocarbons (e.g. esters, alcohols, aldehydes and fatty acids) were removed with the silica gel treatment. Total oil concentration was not significantly different for samples S**3** and S**4**.

4.5.2 Base / Neutral acids

To determine Base/Neutral and acids the experimental runs were carried out by GC–MS using both Full Scan and selected ion monitoring (SIM). From the full scan data the compounds in the standards were identified by their retention indices and the library mass spectra. The retention time of this peak was then compared to that of samples. A typical chromatogram and selected mass spectra are shown in Appendix A figures 4.3 to 4.22. The samples may contain various materials other than the analyses of interest. The presence of these compounds could be related to contamination from the plastic tubes and the absence of the analyses may be losses through evaporation by the steam of nitrogen, on the other hand it could be degraded by bacteria.

Several experimental parameters were found to affect the concentration of the organic acids found in produced water, the acid levels decreased as the brine stimulant became more alkaline.

The organic acids and phenols that make up most of the organic content of produced water have a greater relative density per CH bond than hydrocarbons. This will tend to make infrared determinations that have been calibrated with crude oil yield lower results those by than gravimetric determinations. However, at most, this factor could make only about a 20% difference and has not been found to be a problem (Caudle, 1998).

Corrosion of pipework by produced water containing acetic acid, due to its lower pH, has been confirmed as a potential issue (Joosten *et al.* 2002).

Table 4.10 A list of the retention times and bas peak masses for some Base/Neutral extracted from standard 40:10ng/ml

Compound name	Bas peak masses	Retention time (min)
Acenaphthene	154	22.51
Acenaphthylene	152	21.62
Anthracene	178	29.07
Benzo(a)anthracene	228	41.06
Benzo(k)fluoranthene	252	45.77
Benzo(a)pyrene	252	41.39
Benzo(ghi)perylene	276	50.96
Bis(2-chloroethoxy)methane	172	8.95
Bis(2-ethylhexyl)phthalate	310	42.78
Bis(2-chloroisopropyl)ether	170	10.98
Chrysene	228	41.06
1,2-Dichlorobenzene	146	9.41
1,3-Dichlorobenzene	146	9.41
1,4-Dichlorobenzene	146	9.41
3,3'-Dichlorobenzidine	252	41.39
Diethyl phthalate	222	25.21
Dimethyl phthalate	194	21.89
Di-n-butylphthalate	278	39.57
Di-n-octylphthalate	149	42.78
Fluoranthene	202	34.49
Fluorene	166	9.95
Hexachlorobenzene	284	27.69
Hexachloroethane	201	11.40
Indeno (1,2,3-cd)pyrene	276	50.96
Naphthalene	128	14.62
Phenanthrene	178	29.07
Pyrene	202	34.49
1,2,4-Trichlorobenzene	180	14.45

Table 4.11 Retention times and bas peak masses for some acids extracted from standards 100:10 ng/ ml

Compounds name	Bas peak masses	Retention time (min)
Phenol	94	8.29
2,4-Dimethylphenol	122	12.75
2-Chlorophenol	128	8.29
4-Nitrophenol	139	12.19
2-Nitrophenol	139	21.42
4-Chloro-3-methylphenol	142	16.19
2,4,6-Trichlorophenol 2	196	17.53
2-Methyl-4,6-dinitrophenol	198	17.54
2,4-Dinitrophenol	184	
Pentachlorophenol	266	25.47
Chrysene-12	240	35.91

4.5.3 Volatile organic compounds (BTEX)

Results from the aromatic fraction of volatile aromatic hydrocarbons namely benzene, toluene, ethylbenzene and xylene (BTEX) are presented in Table 4.12. Individual compounds were identified on the basis of their mass spectra. In GC/FID analyses the peaks were matched according to their retention times and using average calculation from the FID chromatogram (Appendix A) shows the calibration graph for standards and the GC chromatogram for the samples, see Figures 4.23 to 4.29.

Table 4.12 Concentrations of volatile aromatic hydrocarbons compounds BTEX (mg/l)

Peak Name	S1	S2	S3	S4
Benzene	0.049	0.078	0.035	0.020
Toluene	0.073	0.108	0.057	0.088
Ethylbenzene	0.003	0.004	0.002	0.002
p+m – Xylene	0.013	0.016	0.012	0.0095
O – Xylene	0.009	0.016	0.010	0.007
Sum BTEX	0.147	0.222	0.116	0.128

The VOCs are the more water soluble hydrocarbon component of the oil (Boylan and Tripp, 1971) and are less likely to be removed from the water by physical oil/water separation. GC analysis of the volatiles (Table 4.12) shows that as benzene is slightly soluble in water it is present in a concentration more than ethylbenzene in all samples. In general BTEX are present in low concentration in all samples. It may stand to reason that biodegradation is relatively rapid for BTEX. BTEX compounds are more volatile and normally will not be detected far away from the discharge point.

4.5.4 Polycyclic aromatic hydrocarbons PAH

The full mass spectrum was analyzed for each peak to provide information on the identity of these compounds quantification of individual compound was determined by peak area measurement and correlated to a standard calibration curve. This is illustrated in Table 4.13 and Figure 4.30 through

Figure 4.38 (Appendix A). Table 4.14 details the results of the GC/MS analysis of all samples.

Table 4.14 Compounds of PAH found by GC–MS (mg/l)

Sample No	Compound	Ion mass	Ppm
S1	Acenaphthene	154	0.95
S2	Acenaphthene	154	2.05
S3	Indeno(1,2,3-cd)pyrene	276	0.47
	Benzo(b)fluoranthene	252	2.24
S4	Benzo(b)fluoranthene	252	0.78

Very low amounts of PAH were found with only three different compounds being identified in the studied samples e.g. acenaphthene (sample**1,2**) indeno(1,2,3-cd)pyrene (sample**3**), benzo(b)fluoranthene (sample **3,4**). One possible reason for this might be the large amount of particulate in the samples since in view of low water solubility of higher molecular weight aromatics in water these compounds could be adsorbed onto suspended particles.

4.5.5 Semi-volatile organic compounds (phenols)

There was no significant variation in the concentration of phenols (Table 4.15) in samples S1 to S3 but sample 4 the value was below the detection limits.

Table 4.15 The concentration of total phenol (mg/l)

Sample No	ppm
S1	0.2
S2	0.2
S3	0.1
S4	> 0.1

4.5.6 Carbon distribution of the oil extracted from the samples

The percent of total area the oil extracted from the samples by related carbon numbers, determined by GC are listed in Table 4.16.

Table 4.16 Carbon distribution of the oil extracted from the produced water samples (Wt. %)

Carbon No	**S1**	**S2**	**S3**	**S4**
C7	5.67	45.02	4.80	7.31
C8	3.3	3.47	3.86	3.87
C9	12.36	7.89	7.91	11.85
C10	9.56	10.33	12.06	17.77
C11	14.89	11.22	17.14	25.64
C12	11.35	8.44	20.62	26.15
C13	8.81	Nd	Nd	Nd
C14	6.33	Nd	Nd	Nd
C15	6.51	Nd	Nd	Nd
C16	3.974	Nd	Nd	Nd
C17	4.67	Nd	Nd	Nd
C18	4.38	Nd	Nd	Nd
C19	2.359	Nd	Nd	Nd
C20	1.68	Nd	Nd	Nd
C21	1.43	Nd	Nd	Nd
C22	2.68	9.19	21.58	7.42
C23	Nd	Nd	Nd	Nd
C24	Nd	4.44	12.03	Nd

(Refer to Appendix A Figure 4.39 to 4.43 for illustrative chromatograms)

Nd = not detected.

The GC/MS analysis was to identify the presence of the groups within chain length C7 to C22 in sample1, and only chain length C7 to C12 was found in all samples. But the chain length C13 to C21 was not identified in the sample (2,3,4). The major straight-chain alkanes groups detected within produced waters are C10 to C30 (Chapelle 1993). The possible explanation is that the chain length in sample 1 is related to diesel range organics (C9 through C28±7) (87), which is similar to chain length of diesel range in crude oil of Al Hamada oilfield (Figure 4.39, Appendix A). The chromatograms in Figures 4.40 - 4.41 shows that the volatile range C5 through C10±2 hydrocarbons that appears in samples 1,2,3,4 could be gasoline range organics (Weisman 1998). A study of the crude oil composition needs to be carried out to confirm this result.

4.5.7 Comparison data

The levels of organic chemicals found in a range of other samples are shown in Tables 4.17.and 4.18 for comparison.

Table 4.17 Organic chemicals in produced water world-wide (mg/l).

Chemical class	**Concentration range**
Total organic carbon	≤0.1 - >11.000
Total saturated hydrocarbon	17-30
Total (BTEX)	0.07-58
Total (PAHs)	0.04-3.0
Total phenols	0.6-23
Total organic acids	≤0.001-10.000

Table 4.18 Organic components of produced water (mg/l) from North Sea data, U.S. data and Hibernia Prediction (Stephenson *et al.* 1994)

Component	North Sea data	U.S. data	Hibernia Prediction
Total Oil (grav)	2 – 220	2.3 – 359	35
Dissolved oil	≤ 760	≤ 200	-
Benzene	0.4 – 5	0.18 - 14.0	3.5
Toluene	0.01- 2	0.16 - 7.95	2.5
Xylene	0.1 – 7	-	0.5
Ethylbenzene	-	0.025 - 0.56	0.3
Naphthalenes	0.07 - 0.1	0.018 - 0.30	0.1
2,4 Dimethylphenol	-	0.016 - 0.57	0.1
Phenol	2 – 23	0.20 - 3.40	1.0
TOC	-	88 – 661	300
COD	130 - 15800	128 – 3000	-
BOD	28 – 6700	126 – 1920	-

The total oil of all samples analysed in this project were found within the results from the range of North Sea and U.S. data in Table 4.18 although the North Sea and U.S. used gravimetric method that measures anything dissolves in the solvent after evaporation such as hydrocarbons , I, IR method used to determine any extracted compounds which have alkyl C-H groups in the molecule. Indeed both methods do not measure the lighter weight compounds (BTEX and naphthalene) in the oil and grease (Weisman 1998).

BTEX compounds although present in low concentration in the Al-Hamada samples studied here are within the normal range in comparison with the data of produced water world-wide in Table 4.17, also the toluene in all samples was found within the range obtained from North Sea data in table 4.18.

The concentration of the **PAH** compounds identified in all samples from the Al-Hamada field were low, agreeing with the normal range from the literature in Table 4.17.

Total phenols measured were at trace levels when compared with the world-wide data in shown in Table 4.17 and are also within the Hibernia Prediction and U.S. Data in Table 4.18. The probable reasons low for levels of phenol and alkyl phenols in produced water are evaporation and/or to degradation by bacteria. It was hoped to employ the GC–MS to identify the Phenol and alkyl phenols compound present; analysis, however, was not carried out due to the time limitation.

4.6 Conclusions

A wide variety of organic pollutants enter the environment in the form of liquids. Measurement of the quantity of oil and grease present in a liquid waste helps in wastewater treatment plant operation and to control the discharge rate.

The identified dissolved organics in the studied samples were a mixture of individual fraction: TOG and TPH, volatile compounds (BTEX), semi- volatile organics phenols, carboxylic acids and high molecular weight aromatic PAHs, The produced water in the studied samples contain more TOG than TPH. None of the compounds of interest were found in Base Neutrals / acid fractions with the exception of the recovery standard and some analytes identified as contaminants. Phenolic compounds were detected at trace levels within the range of 0.1- 0.2 ppm except for sample 4 which was below detection limit. BTEX compounds showed a similar trend to phenol as did PAH. These were found at trace levels in three identified compounds acenaphthene (samples**1 and 2**) indeno(1,2,3-cd)pyrene (sample **3**), benzo(b)fluoranthene (samples **3 and 4**). The reasons for the low concentration level of the dissolved organics probably are that BTEX compounds are volatile, organic acids, BTEX, NPD compounds. Phenol and alkyl phenols in produced water are relatively rapidly degraded by bacteria. Higher molecular weight aromatics PAH have low water solubility. The carbon distribution of the oil extracted from the samples detected were within C_{12} to C_{22}(S1), which could be similar to the diesel range organics in crude oil. C_7 to C_{12} and C_{22},C_{24} (S2 and S**3**), C_7 to C_{12} and C_{22}(S4)

In simple terms, the results indicated that the more positively identified dissolved organic in the studied samples are within the normal range compared to international chemical analysis data (world-wide) & various chemical analysis data of North Sea, U.S. Data and Hibernia Prediction (mg/l level

Chapter 5

Oilfield chemicals (OCs)

5- Oilfield chemicals (OCs)

A varied mixture of oilfield chemicals is added to the topside processing equipment to assist oil–water mixture separation and to avert or decrease operational problems (Grigson *et al.* 2000). Also the quality of the product (crude oil and natural gas), or the effluent can be improved by oilfield chemicals (Offshore Produced Water Waste Management 2001).

5.1 Produced solids

Solids in produced water occur from precipitated solids, silt and sand, such as, propellant that is used in hydraulic fracturing, carbonates, clays, corrosion products, and other suspended solids derived from the producing formation and from well bore process (Veil *et al.* 2004).

The well or the produced water treatment system possibly may be shut down by solids. In particularly these compounds may influence the fate and effects of produced water. Fine-grained solids may decrease the removal efficiency of oil/water separators, leading to discharge limits for oil and grease in produced water being exceeded (Cline 1998). Solids removers (by coagulants and flocculants) are mainly compounds used as reverse emulsion breakers, such as, quaternary polyamines that may be augmented with inorganic iron, zinc or aluminum salts. (Hayward Gordon Ltd).

5.2 Scales

Ions in supersaturated produced water react to form precipitates known as scales when pressures and temperatures are decreased during production. Scales include calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, and iron sulfate (Cline 1998). Scale inhibitors will remain with the produced water due to high solubility in water (Offshore Produced Water Waste Management 2001) and may congest flow lines, generate oily sludges that must be removed, and generate emulsions that are difficult to break down (Cline 1998). The chemical compounds used as scale inhibitors are phosphate esters, phosphonates, and acid polymers (Offshore Produced Water Waste Management 2001). These are used to avoid mineral scale deposition blocking pipe work (Reed and Johnsen, 1996).

Typical treatment concentrations are 3 - 5 ppm. Two methods are used for the addition of scale inhibitors to produced water; squeeze treatments into the producing formation, and continuous injection. (Hayward Gordon Ltd).

5.3 Bacteria

Bacteria, algae, and fungi can be present or be introduced into produced water during water handling processes at the surface. Bacteria may block equipment and pipelines, and also may form difficult-to-break emulsions and hydrogen sulfide (Veil *et al.* 2004). Bacterial degradation of the oil and other products can be avoided by adding biocides and dissolved gases. (Reed and Johnsen, 1996). Bacteria, algae and fungi are controlled by filtration or by adding biocides.

5.4 Treatment chemicals

Many commercial oilfield treatment products are combinations of two or more chemical types. This creates issues for their chemical characterization since only health and safety data are normally specified in material safety data sheets (MSDS) with the details of specific chemicals and quantities contained within the formulation being retained by the manufacturers for commercial reasons (Van Zwol, 1996; Slager *et al.* 1992; Stephenson *et al.* 1994; Flynn *et al.* 1996).

Most of the concerns about the aquatic toxicity of oilfield chemicals concern compounds, such as, biocides, reverse emulsion breakers, and corrosion inhibitors. The aquatic environment receives some or all of these chemicals with the discharged produced water (Van Zwol, 1996; Slager *et al.*1992; Stephenson *et al.* 1994; Flynn *et al.* 1996). Before discharge or injection these chemicals may undergo reactions or processes that diminish their toxicities. For instance, certain chemical reactions lead biocides to lose their toxicity and some corrosion inhibitors never reach the final discharge stream as a consequence of that these chemical measure into the oil phase (Glickman 1998).

In the main treatment chemicals can be sorted into three groups (Stephenson 1992).

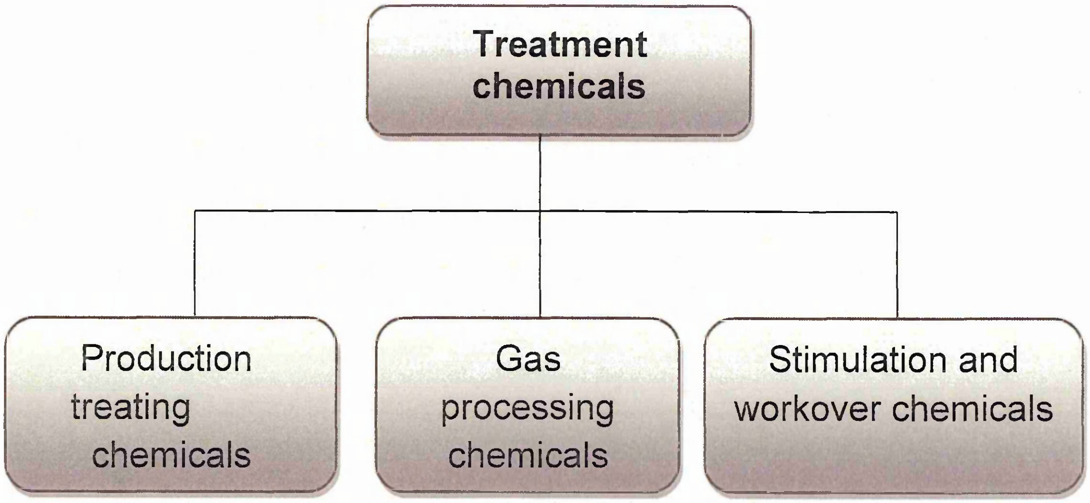

Figure 5.1 Types of treatment chemicals

Table 5.1 Common types of problems and treatment chemicals in offshore oil and gas production operations (Hayward Gordon Ltd).

Problem	Treatment chemicals
Hydrate formation	Hydrate inhibitor
Water vapour	Dehydrator
Chemical corrosion	Corrosion inhibitor
Mineral deposits	Scale inhibitor
Bacterial corrosion	Bactericide
Emulsions (Normal or Reverse)	Emulsion breakers, coagulants, flocculants
Paraffin	Paraffin inhibitor, solvent
Foaming	Defoamer

Usually in gas production hydrate inhibitors and dehydration chemicals are used, while in liquid (crude oil, condensate, water) production, emulsion breakers, coagulants, flocculants, defoamers, paraffin inhibitors and solvents are most generally used (Offshore Produced Water Waste Management 2001).

It is important that the concentrations of the production treatment chemicals used should allow the compounds to travel throughout the treatment system (Offshore Produced Water Waste Management 2001). Normally treatment concentrations in liquid production range between 5 - 15 ppm, while the treatment concentration for gas production may be as high as 100 ppm (Hayward Gordon Ltd).The levels of some of the treatment chemicals are as low as 0.1 parts per million (Glickman 1998) and only trace or very low residual concentrations of these treatment chemical should remain at the point of discharge (Offshore Produced Water Waste Management 2001).

5.4.1 Chemical corrosion

Oil soluble inhibitors get through the oil stream to the refinery, whereas the water-soluble inhibitors stay in the water phase (Offshore Produced Water Waste Management 2001).

5.4.1.1 Corrosion inhibitors

Corrosion inhibitors are used to prevent pipe work from being attacked by salt water (Reed and Johnsen, 1996). Corrosion inhibitor choice is commonly based on the type of corrodent, laboratory or field testing and in addition previous experience. Corrosion inhibitors include four main groups (amine imidazolines, amines and amine salts, quaternary ammonium salts, and nitrogen heterocyclics) and are very complex compounds (Offshore Produced Water Waste Management 2001).

Table 5.2 Commercial oilfield corrosion inhibitors in samples from North Sea oilfields (McCormack *et al.* 2001).

Compound used	**Content**	**Percentage**
CI-D2	Fatty amine quaternary salts as di quaternary and salt and Methanol	10- 30%
CI-C3	Ethoxylated amines and quaternary compounds Butyl glycol Monoethylene glycol	5–10% 20–30% 20–30%
CI-B1	Benzyl chloride quat amine Methanol	5–10% 1–5%
CI-B1	Solvent naphtha (petroleum) Butoxyethanol Long chain alkyl imidazoline	10–15% 1–5% 20–40%

Corrosion of pipework was discovered in the Romania, California and Russia fields from refining of oils in the 1920s.

The concentration of active components in most corrosion inhibitors is usually 30 - 40% (Offshore Produced Water Waste Management 2001). However the concentration of oil soluble corrosion inhibitors is fairly low in discharged produced water e.g. low levels of benzylalkonium quaternary ammonium salts

(0.74-10.84 ng/g). Typical corrosion inhibitor chemicals were found in marine sediments in the proximity of two North Sea oil platforms (Grigson *et al.* 2000).

5.4.1.2 Hydrate inhibition

In the presence of water under certain thermodynamic conditions, usually high pressure and low temperature, natural gas hydrate (an ice-like solid) occurs. Gas wells are usually shut off at the inception of significant water production because of the risks from hydrates (Offshore Produced Water Waste Management 2001).

Hydrate inhibitor and dehydration chemicals are solely used in gas production. Pieces of hydrate moving through pipes can plug piping, stopping fluid flow, or equipment. Typical chemicals used for hydrate inhibition are ethylene glycol and methanol. About half of the methanol used for hydrate inhibition will stay in the discharged water stream, while the rest vaporizes into the gas. Its treatment concentrations typically range between 5–15 gallons per million cubic feet of produced gas for both methanol and ethylene glycol (Offshore Produced Water Waste Management 2001).

5.4.2 Dissolved gases

Oxygen inhibitors (scavengers) are composed of sulfite, primarily as ammonium bisulfate (Offshore Produced Water Waste Management 2001).

Oxygen scavengers and other treatment chemicals are used to reduce levels of undesired dissolved gases like carbon dioxide, and hydrogen sulphide (Veil *et al.* 2004). The concentration that oxygen scavengers are used at is less than 100 ppm and they are not consider as toxic since seawater contains about 2,700 ppm sulfate (Offshore Produced Water Waste Management 2001).

5.4.3 Bactericides

The most usual biological problem found in oil and gas production facilities are sulfate reducing bacteria (SRB). SRB reduce the sulfate ion to hydrogen sulfide, which is the main cause of chemical corrosion, steel embrittlement, and fouling of equipment by the formation of iron sulfide. Three types of chemicals (quaternary amine salts, amine acetates, and glutaraldehyde) are used as bactericides in offshore production operations (Offshore Produced Water Waste Management 2001).

Bactericides are highly water soluble and are sold as aqueous solutions with bulk concentrations ranging from 10% - 50%. Bactericides concentrations will be between 100 – 200 ppm for 2 –6 hours through slug treatments and range between 5 – 20 ppm with continuous treatment (Offshore Produced Water Waste Management 2001).

5.4.4 Dehydration

Triethylene glycol (TEG) is employed offshore to eliminate the water vapor from natural gas. The TEG is heated to more than the boiling point of water to separate it from condensed water by distillation processes, and then discharged even though it contains small amount of TEG (Offshore Produced Water Waste Management 2001).

5.4.5 Mineral deposits

Severe consequences can result from the deposition of inorganic mineral compounds onto the metal surfaces of production equipment. These include; perforations in production tubing, increasing operating temperatures (in heater tubes), increasing pressures and reduced efficiency (Offshore Produced Water Waste Management 2001).

Calcium carbonate, calcium sulfate (gypsum), strontium sulfate, and barium sulfate, are the main mineral scales. These are controlled by using chemical treatment and the chemicals used for this purpose, work by interfering with crystal growth (Offshore Produced Water Waste Management 2001).Typical treatment concentrations are 3-5 ppm (HAYWARD GORDON LTD).

5.4.6 Emulsion breakers

Two types of emulsions are used in oil production. These are normal emulsions (oxyalklated resins, polyglycol esters, and alkl aryl sulfonates) and reverse emulsions (polyamines, polyamine quaternary compounds polyacrylates and thiocarbamates). Water droplets are dispersed in the continuous oil phase in a normal emulsion, whereas in reverse emulsion oil droplets will suspended in the continuous water phase (Offshore Produced Water Waste Management 2001), Emulsion breakers are used to facilitate oil–water separation (Reed and Johnsen 1996). These materials are water soluble and will stay with the separated solids, which are not usually discharged (Offshore Produced Water Waste Management 2001).

Equally naturally occurring materials like solids, resins, asphaltenes, and organic acids in the produced fluids as well as introduced materials like corrosion inhibitors, bactericides, and corrosion inhibitors increase emulsion stability (Offshore Produced Water Waste Management 2001).

Emulsion breakers typically exist in concentrations of 30 - 50%. Emulsion breakers are added continuously to the production system at concentrations ranging from 10 - 200 ppm for normal emulsion breakers and between 5 – 15 ppm (based on water) for reverse emulsion breakers (Offshore Produced Water Waste Management 2001).

Owing to the low concentration of oil reverse emulsion treatment is more problematic (Hayward Gordon Ltd).

5.4.7 Defoamers

In produced water treatment, advantages of the use of foam depends on its amount; it may be a benefit as in gas flotation cells or it can be a trouble as it makes subsequent handling of the recovered waste stream more difficult (Offshore Produced Water Waste Management 2001).

Only small amounts of defoamers are discharged in produced water since they will stay with the recovered oil froth that is returned to the produced oil stream (Oil & Gas Industry-Produced Water Chemical Treatment 101).

Silicones and polyglycol ester-based compounds are used for controlling foam. These compounds work by disrupting the gas/liquid interface therefore breaking down the foam, but the solubility is very low in oil and water (Offshore Produced Water Waste Management 2001).Typical treatment concentrations are 5 -25 ppm (Hayward Gordon Ltd).

5. 5 Techniques used for the analysis of oilfield chemicals

Studies of the operational use and environmental fate for the levels of oilfield chemicals in oil production chemicals and produced waters have been previously carried out by electrospray-ionisation ion trap-mass spectrometry (ESI-MS/MS) coupled with liquid chromatography, and also by wet chemical analysis techniques (Grigson *et al.* 2000).

ESI-MS/MS is a very important technique for the identification of polar chemicals that are used as demulsifiers, corrosion inhibitors and biocides, e.g.

imidazolines, alkylbenzene sulfonates, quaternary ammonium compounds (quats) and ethoxylates (Gough and Langley, 1999). In particularly, corrosion inhibitors that partition primarily into the aqueous phase and demulsifiers into the oil phase have been studied in this way (Grigson *et al.* 2000).

The production chemical usages in the Al Hamada oilfield are scale inhibitors, different types of biocide & corrosion inhibitors and raw water treatment. With the limited time available for this project only two types of oilfield chemical were eventually selected (chemicals used at the time when the samples were collected) for the determination amine group (active group) in corrosion inhibitor and biocides by analytical methods, Electrospray ionization tandem mass spectrometer (ESI-MS/MS), that is a sensitive technique and the parent –daughter ion analysis (MS/MS) is very specific as it avoids incorrect identification of peaks in the produced water.

5.6 Materials and methods

5.6.1 Instrumentation

Mass spectral analysis was carried out using an Applied Biosystems /MDS Sciex API365 triple quadrupole mass spectrometer fitted with a Turbo ion spray heated and assisted electrospray ion source.

5.6.2 Proprietary oilfield chemicals

Two Proprietary oilfield chemicals (one corrosion inhibitor, one biocide & corrosion inhibitors) were supplied by Al Hamada oilfield operators:

corrosion inhibitors EC1295 , biocides and corrosion inhibitors EC 6202

5.6.3 Preparation of oilfield chemicals standards

Proprietary corrosion inhibitors and biocide (50 mg) were diluted to 50 ml with methanol. Proprietary oilfield chemicals were then analyzed by ESI-MS/MS for the components, of interest.

5.6.4 Sample preparation

Prior to analysis by ESI-MS/MS 200 ml from each of four samples were extracted with dichloromethane (DCM) three times (3x50) and the extract was evaporated under a gentle stream of nitrogen and the residue re-dissolved in 500µl:250µl (v/v) MeOH: H_2O. Again the samples were extracted with dichloromethane (DCM) and reduced to 1 ml then divided into two portions and dried, one of them re-dissolved in methanol to 1 ml while the other in 1000 µl acetonitrile. Finally the samples were subjected to ESI-MS/MS to look for the presence of the components of interest, where selected masses were detected by the MRM mode, i.e., parent/daughter ion transitions. The observed result was further confirmed by analysis with HPLC coupled with ESI-MS (LC-ESI-MS).

To put it briefly prior to analysis by LC-ESI-MS commercial mixture of oilfield chemicals 1ml corrosion inhibitors, 1ml biocide, 1ml scale inhibitors, 1ml Demulsifies were typically made up to 50 ppm in methanol.

500 ml of produced water samples were extracted with DCM and the solvent was evaporated and the residue re-dissolved in acidified methanol [90:10 (v/v) MeOH: water]. Then all isolated chemicals of interest were subjected to mass spectrometric analysis using a Finnigan Mat LCQ (San Jose, CA, USA.). Reversed-phase HPLC separations were performed using LC equipped with a pumping system and detector and coupled with electrospray ionisation mass spectrometry (ESI-MS). The eluent was a mixture of methanol and

water [90:10 (v/v) MeOH: water] and the column was a reverse phase C18 (Phenomenex 15 cm x 1.0 mm).

5.7 Results and discussion

Most of the oilfield chemicals have a commercial name related to the manufacturing company. However only a few oilfield chemical 'active constituents' are used in the pure form, most are formulated as mixtures.

5.7.1 Standard quaternary ammonium compounds

Preliminary results obtained from the oilfield and produced water studied showed that quaternary ammonium compounds (Quats) were important constituents, since positive ion ES-MS mass spectra were observed. These quaternary ammonium compounds (Quats) are cationic surfactants and are broadly used as corrosion inhibitors and biocides. In fact the monoalkyl quats are biocide ingredients and a little surfactant while twin chain (long) quats used as surfactants but do not have biocide activity. Typical quat formulations are derived from tertiary Coco amines as the starting materials. These amines are then quaternised by reactive alkylation. Reagents, such as, benzyl chloride or dimethyl sulfate are used to produce the charged species. Thus ES-MS can be used to qualitatively characterize different classes of quaternary ammonium and imidazoline/amide based corrosion inhibitors with relative ease.

5.7.2 Studies of proprietary oilfield chemicals formulations

The spectrum of the results for oilfield and produced water studied is shown in Figure **5.2** positive ES-MS/MS mass spectra have been obtained for quaternary ammonium compounds (benzylalkonium chloride), the four ion peaks of ESI-MS/MS analysis of the precursor ion are *m/z* 304.4,332.4,360 for corrosion inhibitors (EC1295) and biocide & corrosion inhibitors (EC 6202). These masses represent the molecular ions of the C12 and C14 alkyl chain components, respectively in the mixture.

5.7.3 Studies proprietary of residues of oilfield chemicals in samples

Comparing the results from produced water studied to the ESI-MS mass spectra obtained from oilfield EC1295 & EC 6202 samples, there was some of the variation between the ion obtained ,the precursor ion *m/z* 304.4,332.4,360 obtained in most of the samples in various solvents (e.g. methanol, acetonitrile and methanol/water), see Figures **5.3, 5.4** and **5.5.**These masses represent the molecular ions of the C12, C14 and C16 (respectively) alkyl chain components in the mixture. In other samples as well as in the quats a chromatographic peak at m/*z* 359 is obtained in S1 and S4 for the methanol/water fraction and for the acetonitrile fractions of S1, S3 and S4. C16 did not appear clearly in the oilfield (EC 6202) sample, this meant the sample may need further cleaning from possible contaminants. The additional clean-up of the sample may be obtained by coupling solid phase microextraction with HPLC.

This was confirmed by running the oilfield and sample extracts by LC-ESI-MS see Figures **5.6 and 5.7** which all gave reproducible mass spectra for *m/z* 304, 332, 360 and 388, which correspond to the molecular ions of the C12, C14, C16 and C18 respectively.

Comparing the two methods it was found that all samples have been extracted contained corrosion inhibitors EC1295, biocide & corrosion inhibitors EC 6202 (an aqueous blend containing quaternary ammonium compound).

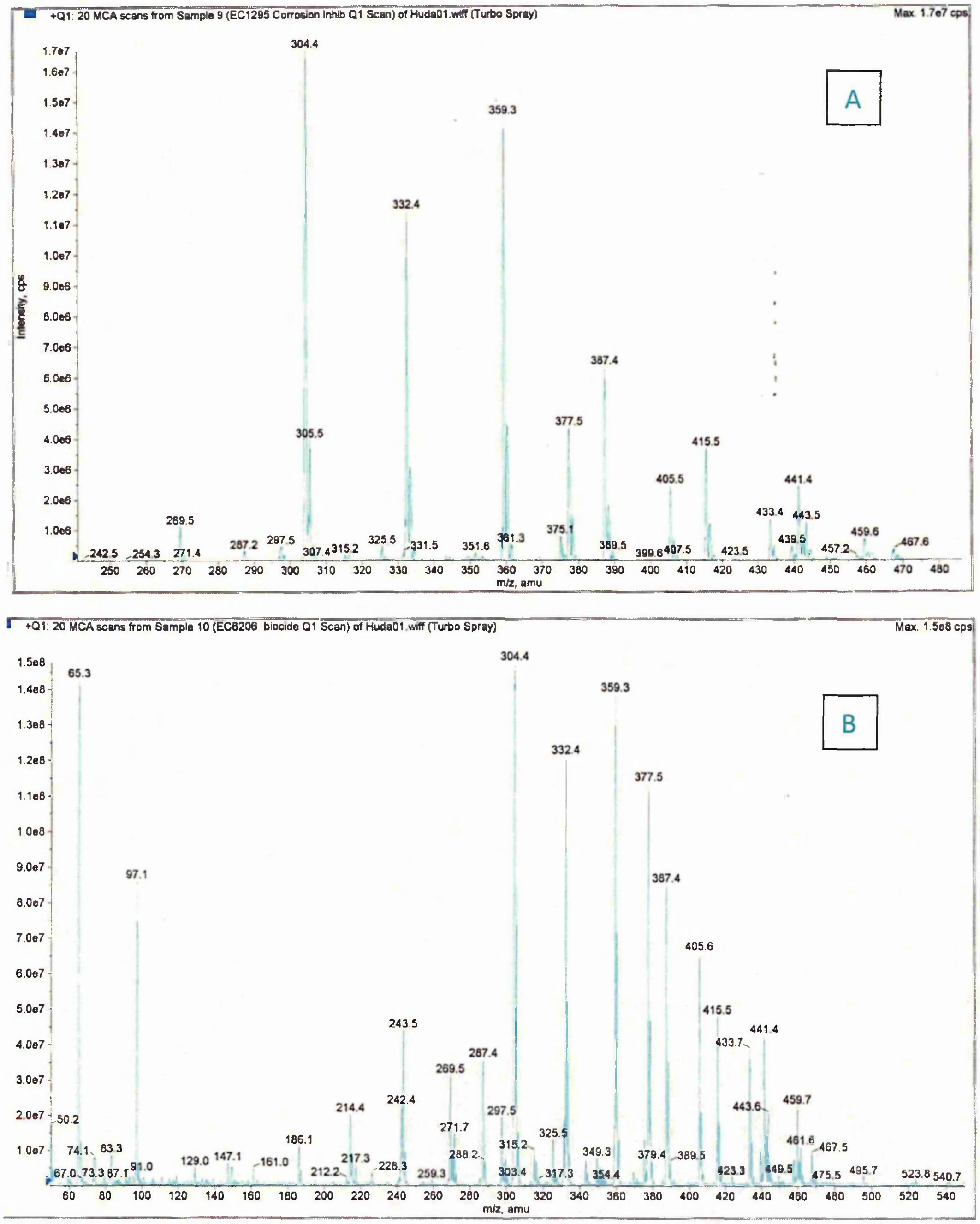

Figure 5.2 ESI-MS/MS mass spectra of (A) a proprietary corrosion inhibitor (EC1295) and (B)biocide and corrosion inhibitors (EC 6202) (1 : 1 v/v MeOH:H_2O)

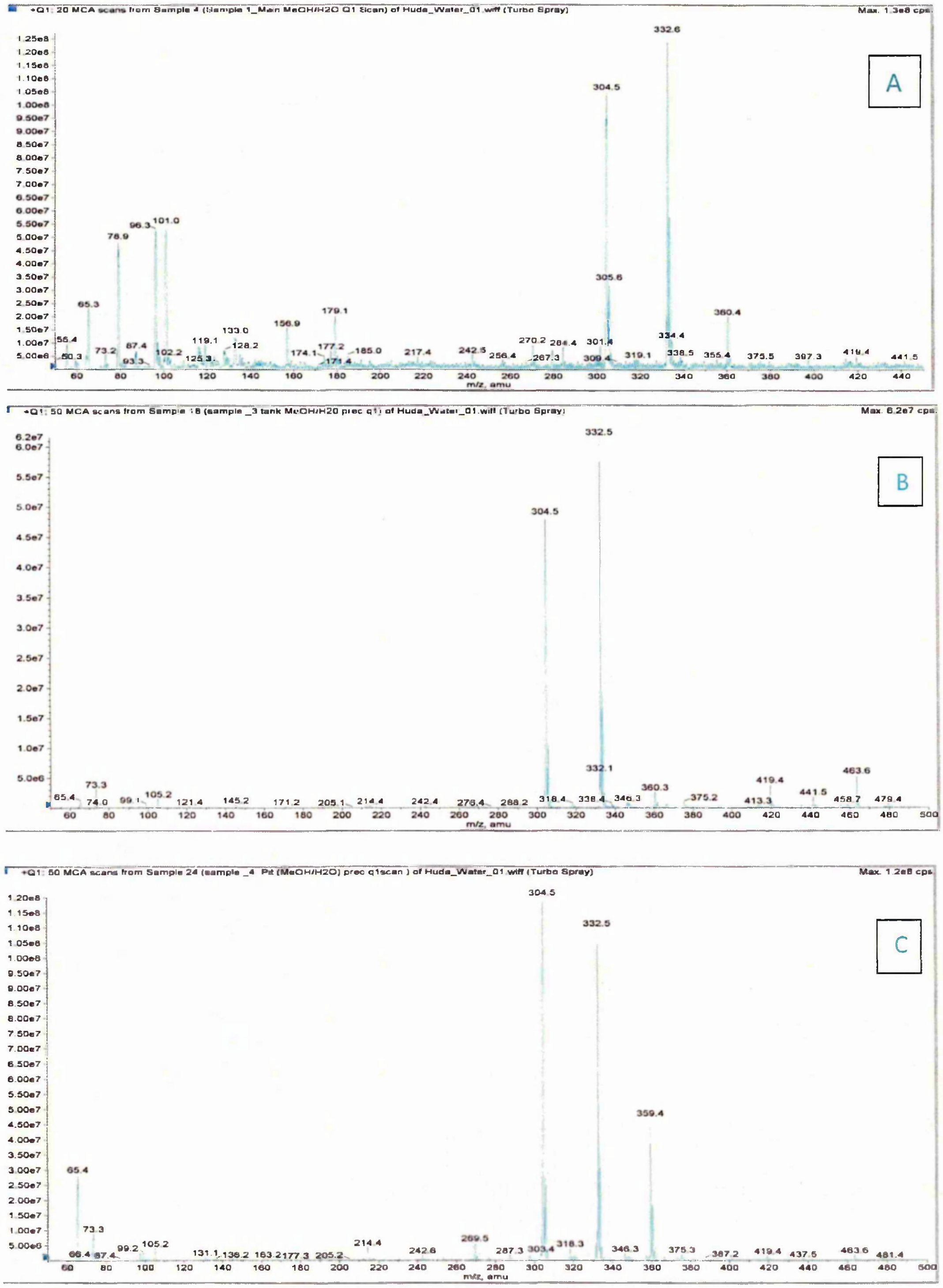

Figure 5.3 ESI-MS/MS mass spectra of ions (*m/z* 304) and (*m/z* 332) in produced water extract (A) Sample1, (B) Sample3, (C) Sample4: (MeOH:H_2O)

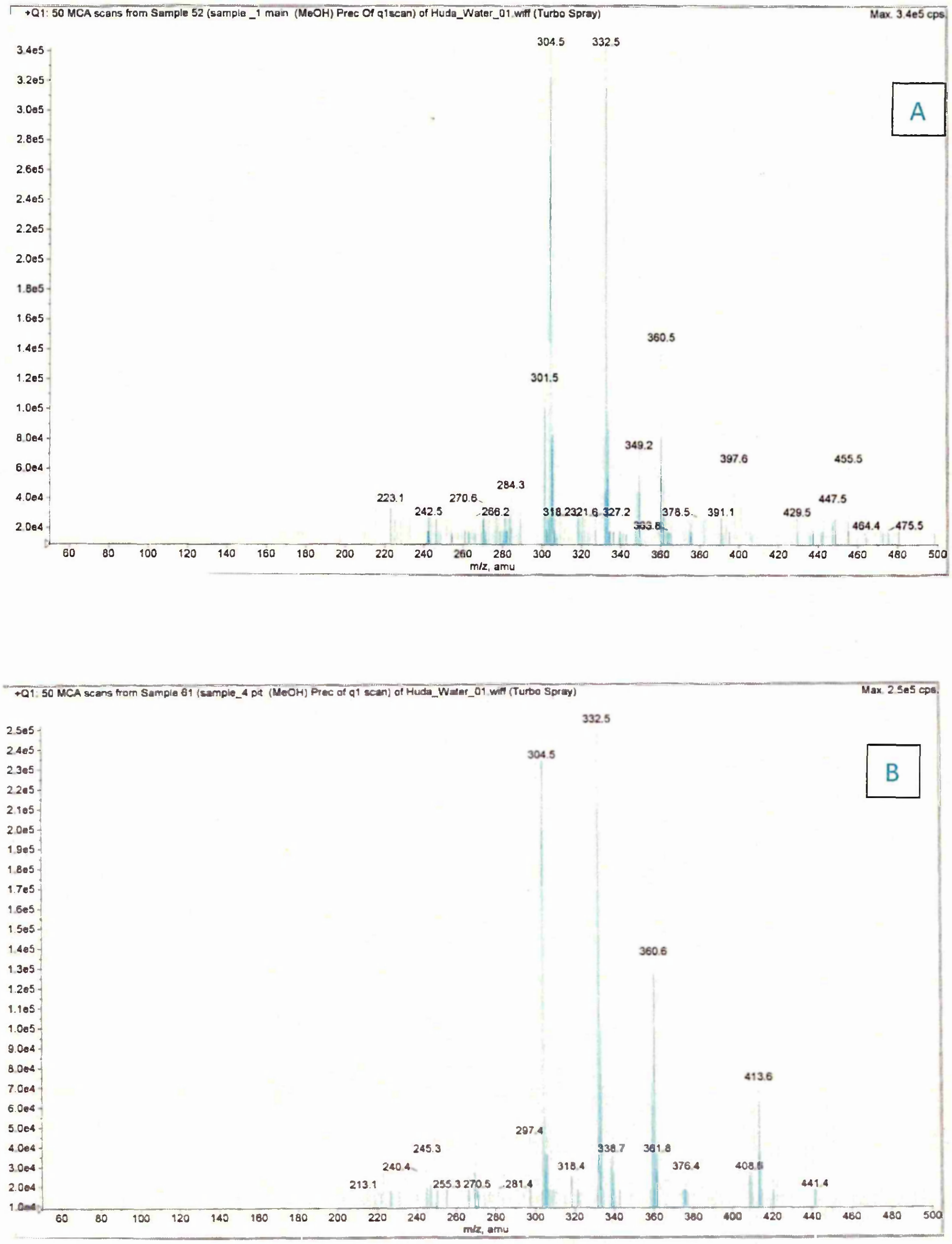

Figure 5.4 ESI- MS/MS mass spectra of ions (*m/z* 304), (*m/z* 332) and (*m/z* 360) in produced water extract (A) Sample1 and (B) Sample4: MeOH solvent

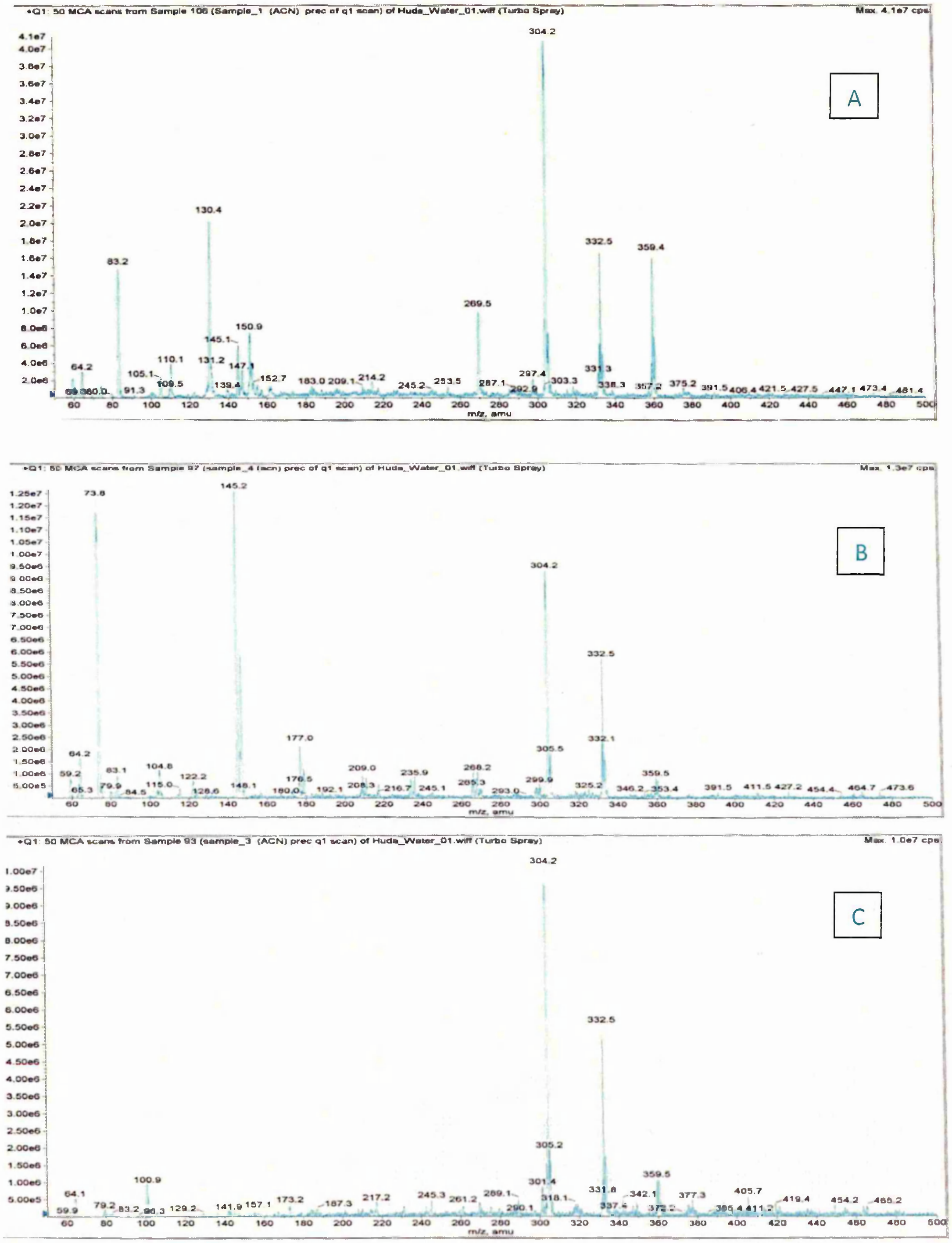

Figure 5.5 ESI- MS/MS mass spectra of ions (*m/z* 304) and (*m/z* 332), in produced water extract (A) Sample1, (B) Sample3, (C) Sample4: ACN Solvent

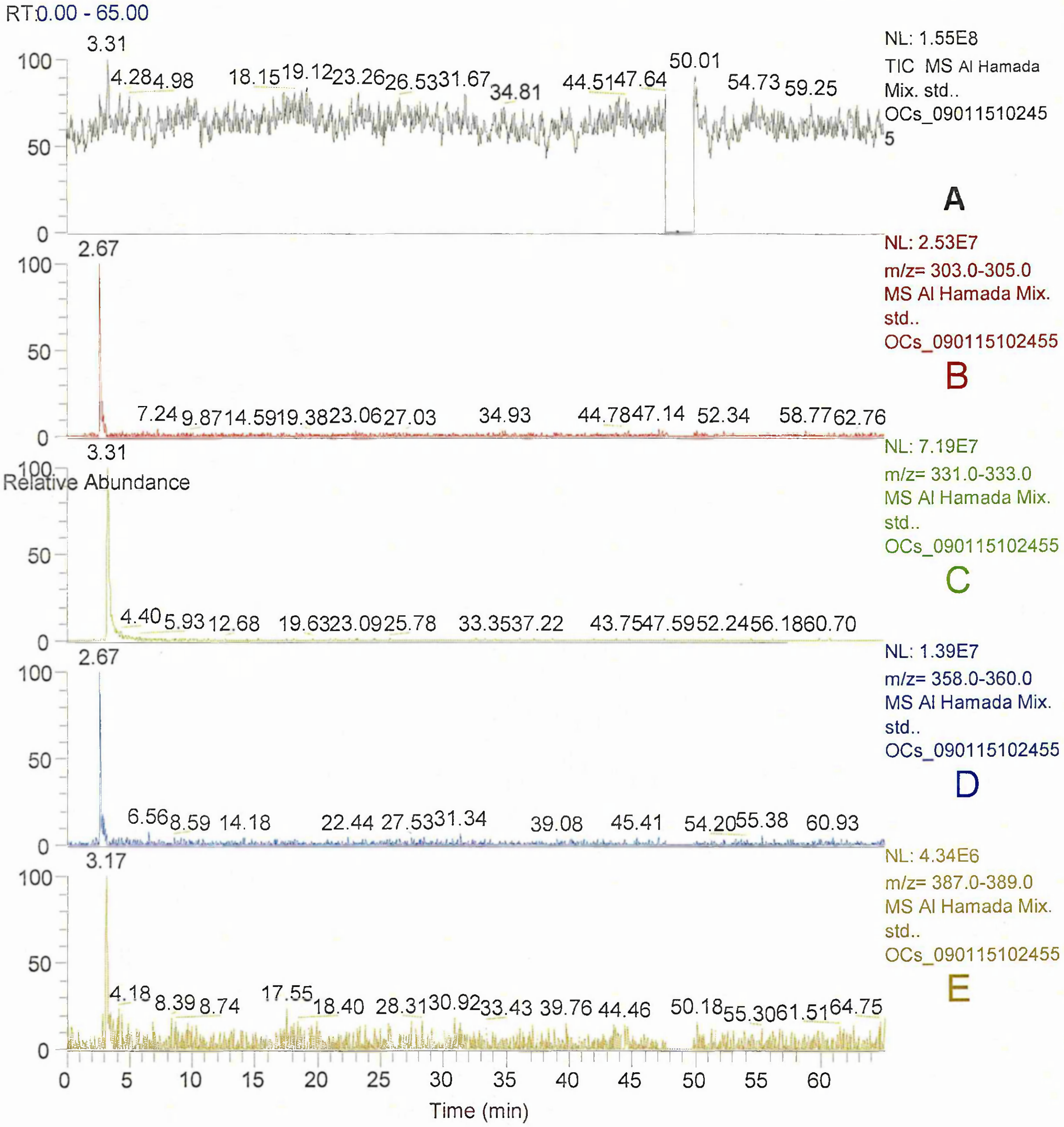

Figure 5.6 Chromatograms of quaternary ammonium compounds obtained by LC/ESI-MS analysis of mixed standard (A) Full Scan 50-1850 (B) mass range 303-305 (C) mass range 331-333 (D) mass range 358-360 (E) mass range 387-389

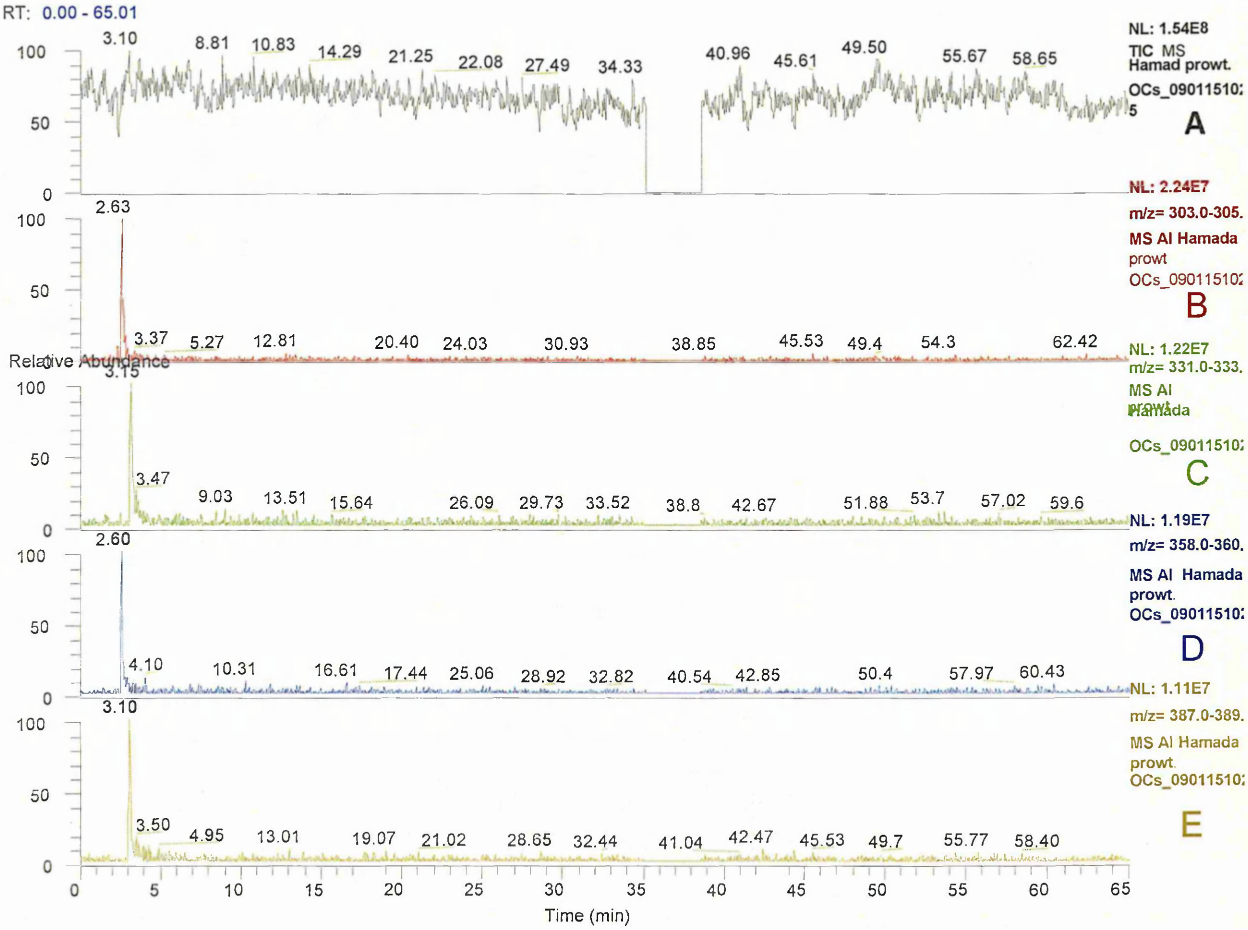

Figure 5.7 Chromatograms of the produced water samples by (LC-ESI-MS) (A) Full Scan 50-1850 (B) mass range 303-305 (C) mass range 331-333 (D) mass range 358-360 (E) mass range 387-389

5.8 Conclusion

Oilfield chemical corrosion inhibitor (1995 A) and corrosion inhibitor and biocide (6206A) compounds and residues which discharge with produced water have been qualitatively examined by electrospray ionization tandem mass spectrometry (ESI-MS/MS) in various solvents, e.g. methanol, acetonitrile and methanol/water) The results were confirmed by coupling ESI-MS and HPLC, (LC-ESI-MS) in methanol/water.

Corrosion effects come from chemical reaction or the effects of microorganisms, as most of chemistry of the corrosion inhibitor chemicals is amine-based (amine imidazolines, amines and amine salts, quaternary ammonium salts, and nitrogen heterocyclics). The interest is focused on the determination of amine groups, the active ingredient in corrosion inhibitors. In addition to controlling the growth of both aerobic and anaerobic bacteria, in particularly, sulfate reducing bacteria (SRB) the biocide chemical is added, the formula of which contains a blend of quaternary ammonium salts. Furthermore by improving solubility in water, soluble corrosion inhibitors, such as quaternary amines, can be used.

Quaternary ammonium compounds (quats) were detected in oilfield chemicals and all produced water samples, which represent molecular species with alkyl chain lengths of C12 (*m/z* 304), C14 (*m/z* 332), C16 (*m/z* 360), but C18 (*m/z* 388) only appeared by (LC-ESI-MS).

The presence of production chemicals in produced water may make a smaller contribution to toxicity of produced water discharges than other pollutants, but chemicals which are classified as highly toxic may not actually present an acute toxicity threat to the marine environment. However the hydrogen sulfide poses the most significant risk to human health and the environment.

Chapter 6

Conclusion and recommendations

6 - Conclusion and recommendations:

6.1 Conclusion

An attempt has been made to investigate the compounds that contribute to the environmental impact of produced water from the Al Hamada oil field Libya. The chemical composition of this produced water was characterized using a variety of analytical techniques.

The results of physiochemical property testing showed that there are minor variations in alkalinity, hardness, and pH at all four of the sampling spots chosen. TDS and COD were believed to be at a normal level in produced water. Metals were detected-slightly above the ICP detection limit in all samples, including barium, iron, manganese, lead, and zinc, (which is regarded as a toxic metal). Only moderate differences were observed in the concentrations between these metals from the sites chosen. The highest value of metal detected was for barium, and this is probably due to the precipitation of barium sulfate scale. The heavy metals content in the samples are consistent with those mentioned in the literature except for manganese which was higher in the concentration range 0.06-0.23 ppm.

The hydrocarbon content of this produced water is managed (removed) by an efficient skimmer-recycling pound system, before being discharged to the pits, but dissolved hydrocarbons are considered to be a serious threats for all kinds of life due to their toxicity and carcinogenicity. The TPH contents in these samples were lower that of TOG. Acids were not detected in the tested samples in Base Neutrals / acids fractions. BTEX, NPD compounds, phenol and alkyl phenols are relatively rapidly degraded by bacteria, so it was not surprising that the phenolic compounds, BTEX and PAH were detected at trace levels within range 0.1- 0.2 for BTEX and PAH and 0.4 - 2 ppm for PAH in three identified compounds acenaphthene, indeno (1,2,3-cd)pyrene, benzo (b) fluoranthene in these samples. The carbon of the oil extracted from the samples was distributed between the low and mid-range carbon masses, The organic compounds in produced water studied are within the normal range compared to international chemical analysis data (world-wide) and various chemical analysis data of North Sea, U.S. Data and Hibernia Prediction (mg/l) (Tables 4.17.and 4.18).

Analyses of one corrosion inhibitor and one combined corrosion and biocide inhibitor of oilfield chemicals and produced water samples showed relatively few chemicals with active amino groups {quaternary ammonium compounds (quats)} which represent molecular species with alkyl chain lengths of C12 (*m/z* 304), C14 (*m/z* 332) and C16 (*m/z* 360) were detected by electrospray ionization tandem mass spectrometry (ESI-MS). There were no appreciable differences in results obtained by coupling ESI-MS with liquid chromatography HPLC, (LC-ESI-MS) in methanol/water in addition to above m/z only C18 (*m/z* 388) had appeared.

The conclusion is that the most important groups of components leading to the toxicity of produced water are the organic material (e.g. hydrocarbons and phenols), the heavy metals, and the major ions responsible for the salinity and osmotic properties of the water, which were in the samples studied at moderate levels, likewise the level in produced water in the literature (Table 4.18).

The residual oilfield chemicals that have been detected in produced water samples need to be tested for toxicity (Acute and chronic toxicity).

6.2 Recommendations:

The most crucial recommendations that have to be taken seriously for the produced water are:

- It should not be consumed by humans and animals.
- It should not be used for irrigation of crops or plants. The irrigation of green grass and non-fruit bearing plants is useful but these plants should not be consumed by humans and animals.

Future investigation studies should be carried out on the groundwater in the field to check whether it is polluted with the oilfield chemicals before consumption.

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Appendix A

- Calibration Graph of Standards
- Chromatograms of standards and samples
- Structure of Quaternary Ammonium Compounds (Quats) C12, C14, C16

Table 4.9 Concentration and absorbance for standard solutions (TPH&TOG)

Concentration (mg/l)	Absorbance
0	0
26.85	0.10
71.6	0.25
147.7	0.48
300	0.84
600	1.08
1000	1.50

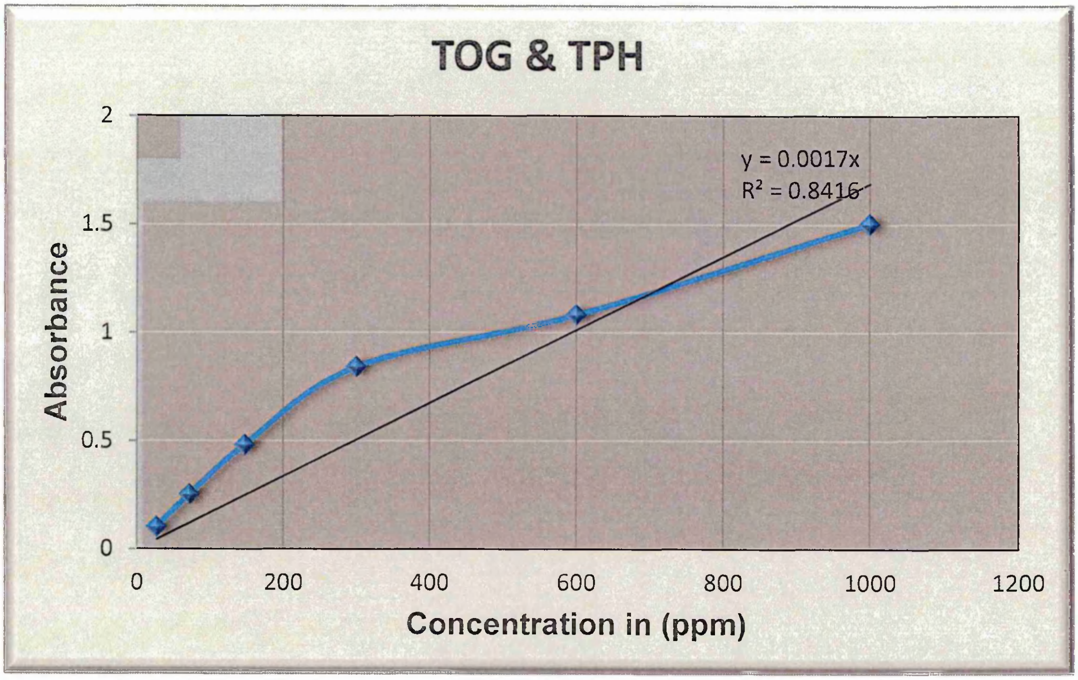


Figure 4.2 Calibration Graph of infracal instrument used to determine TPH and PAH

```
Misc Info   : 40ng/10ng
Vial Number: 1
```

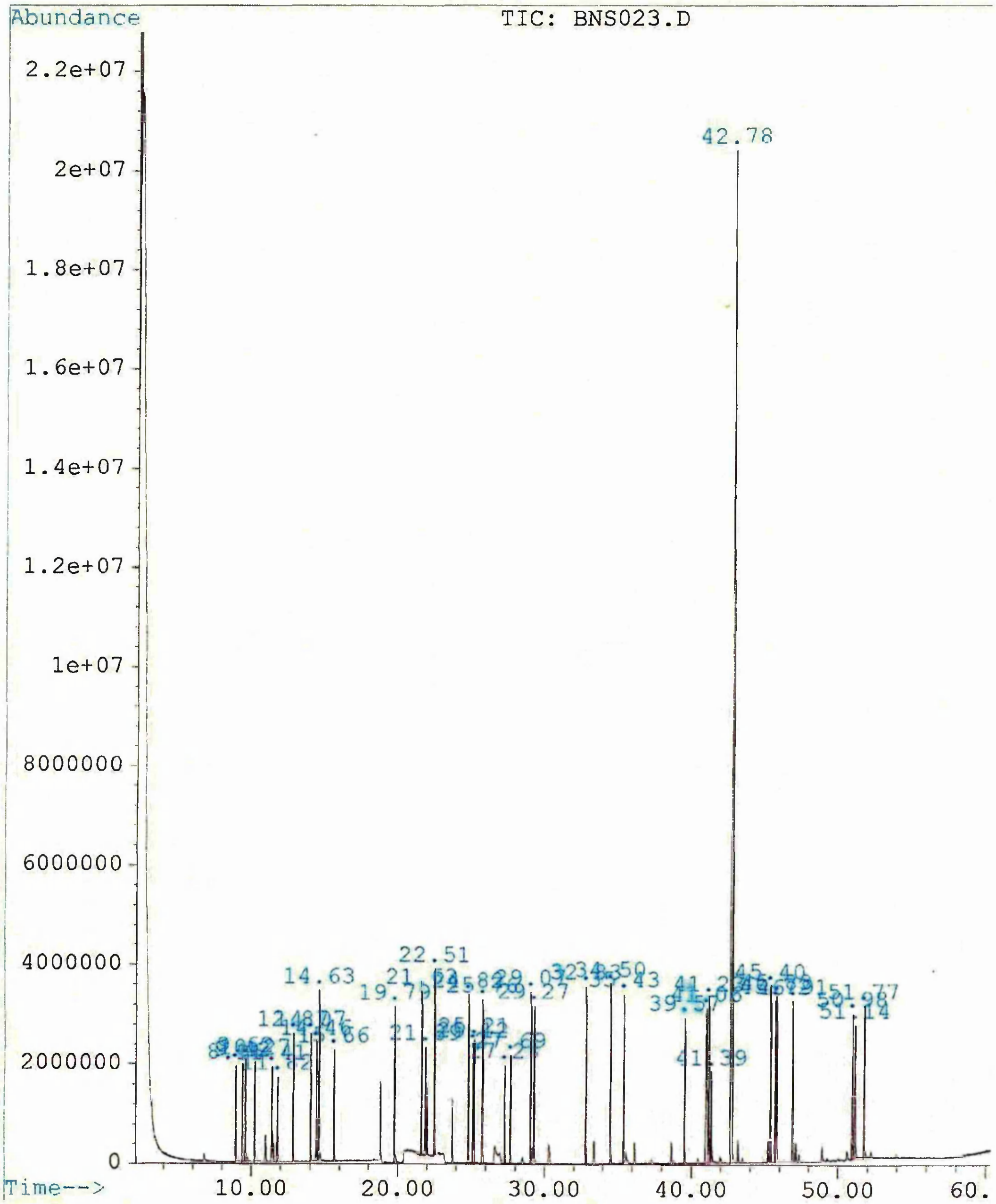
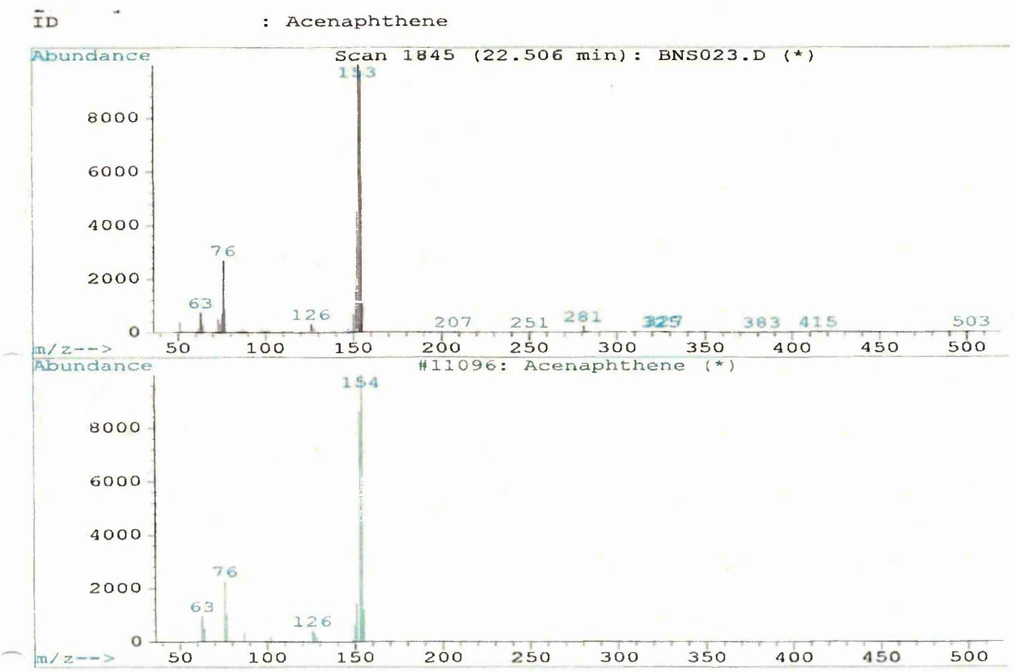


Figure 4.3 Total ion chromatogram (TIC) of the Base/Neutral fraction extracted from standard (40:10ng/ml)



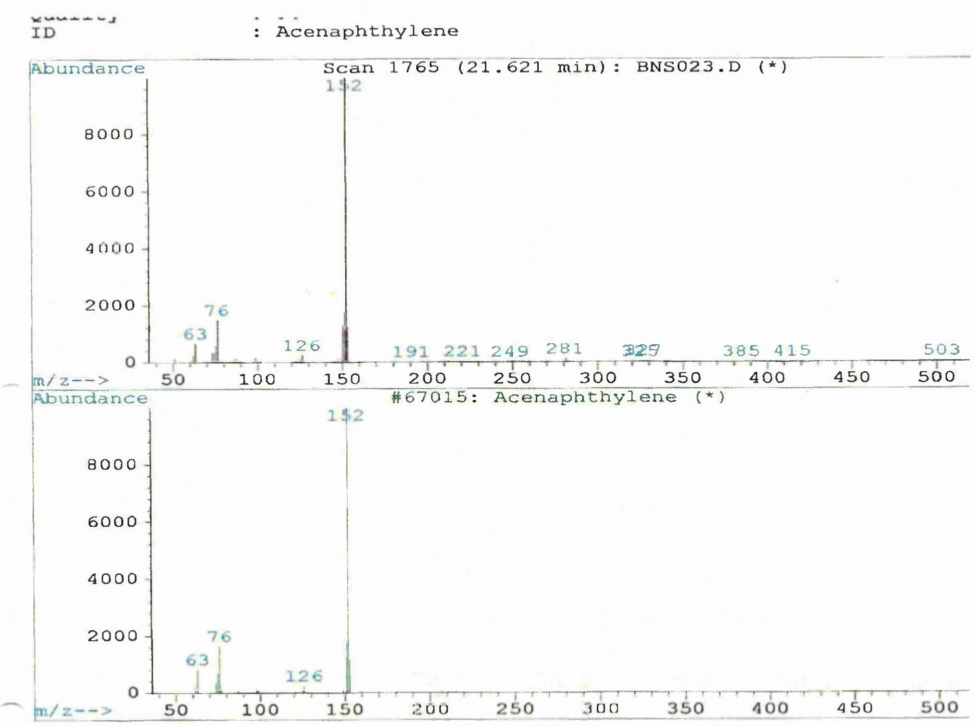


Figure 4.4 Mass spectra of acenaphthene and acenaphthylene in standard of Base/Neutral fraction.

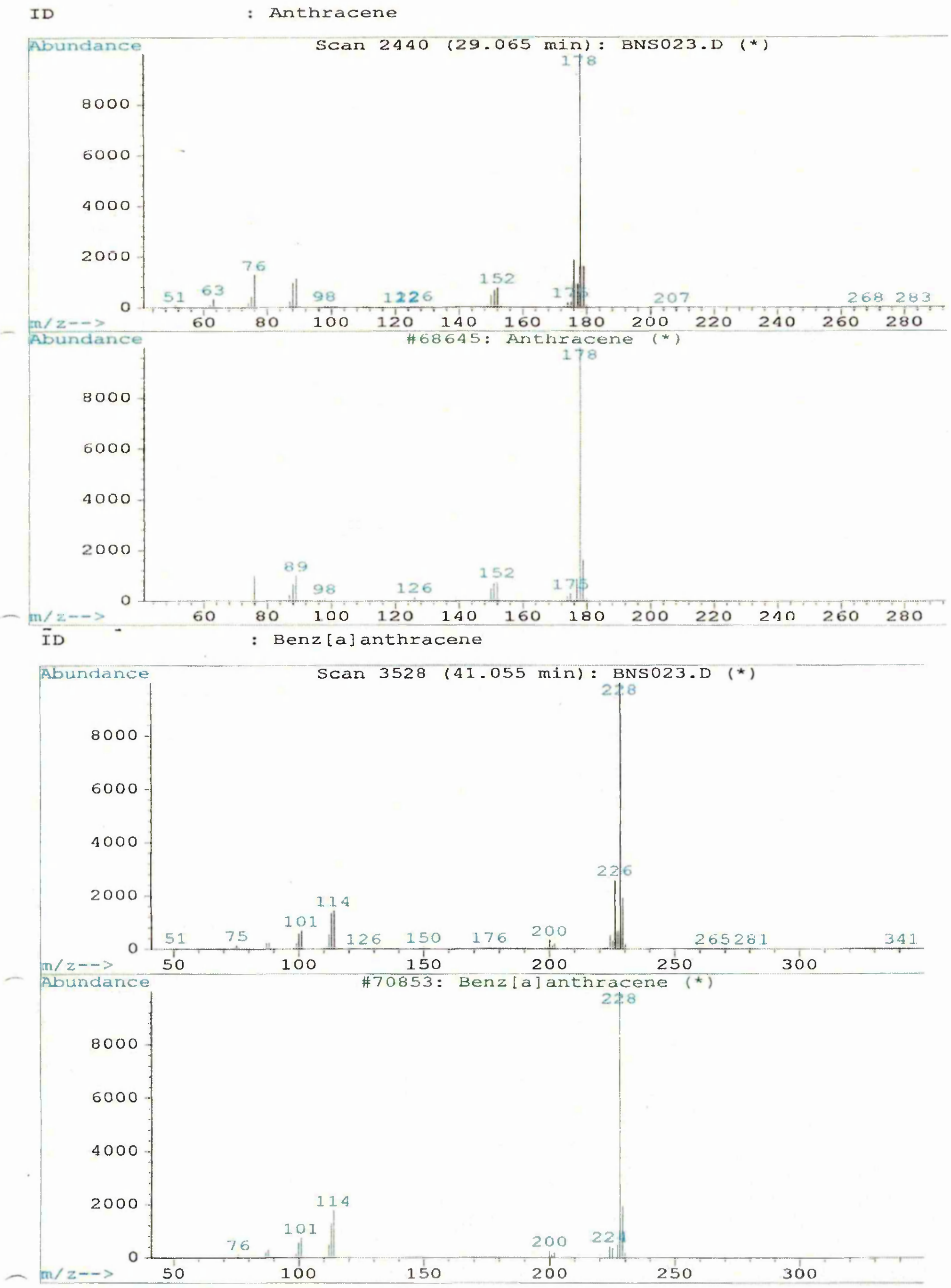
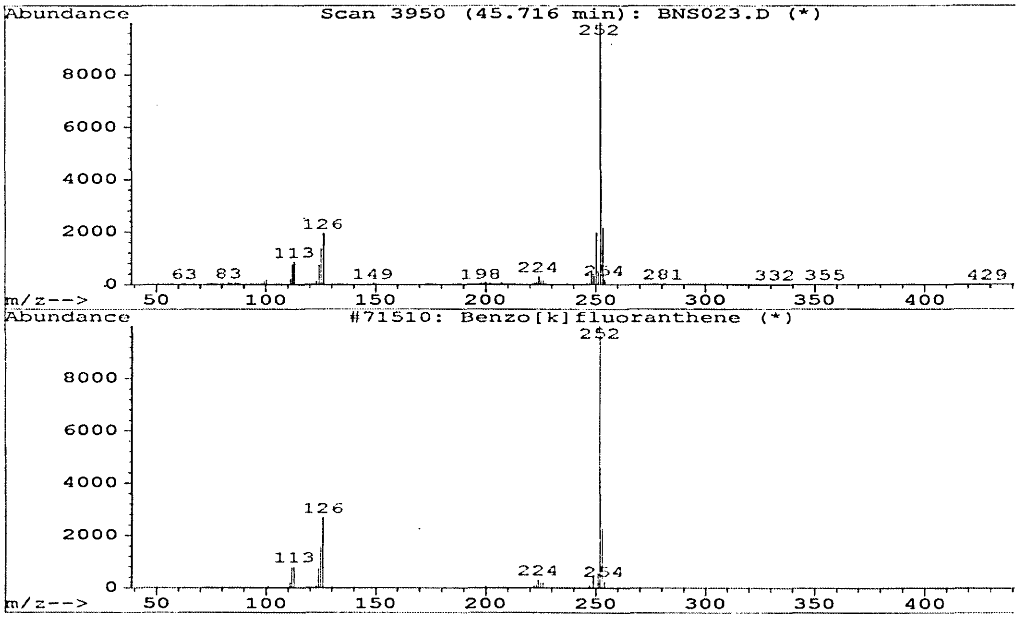


Figure 4.5 Mass spectra of anthracene and benzo(a)anthracene in standard of Base/Neutral fraction.

ID : Benzo[k]fluoranthene



ID : Benzo[a]pyrene

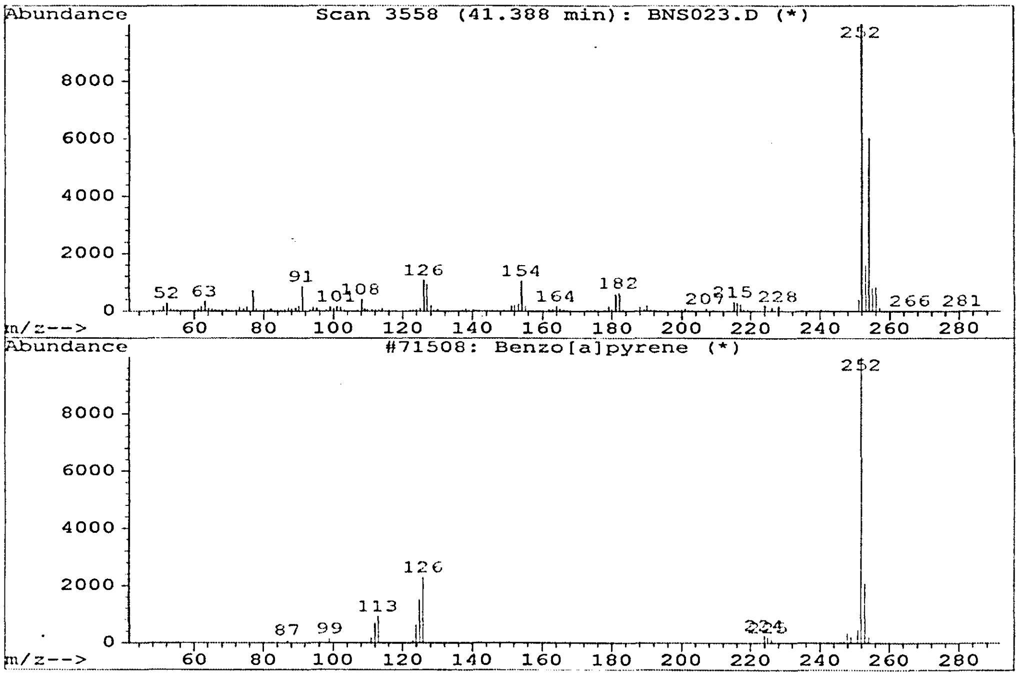
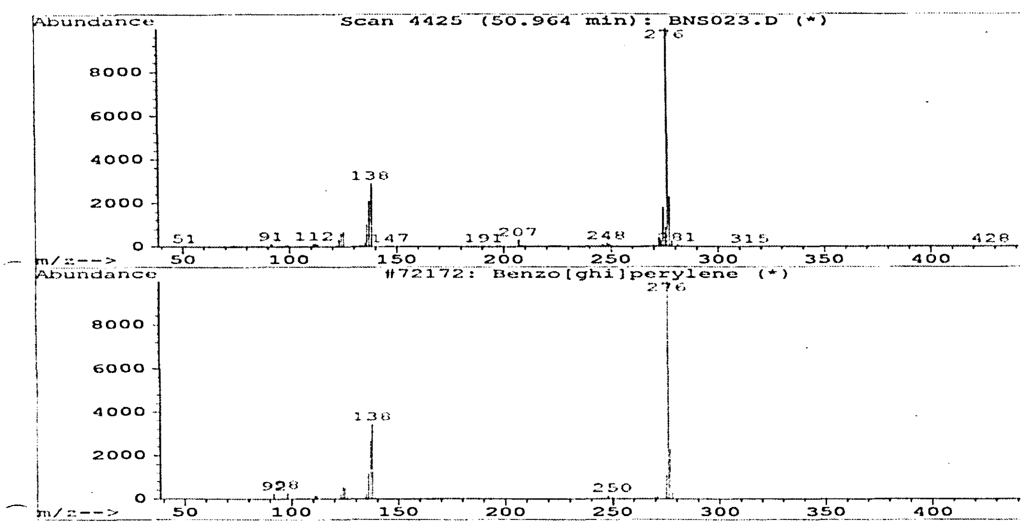


Figure 4.6 Mass spectra of benzo (k) fluoranthene and benzo (a) pyrene in standard of Base/Neutral fraction.

ID : Benzo[ghi]perylene



ID : Methane, bis(2-chloroethoxy)-

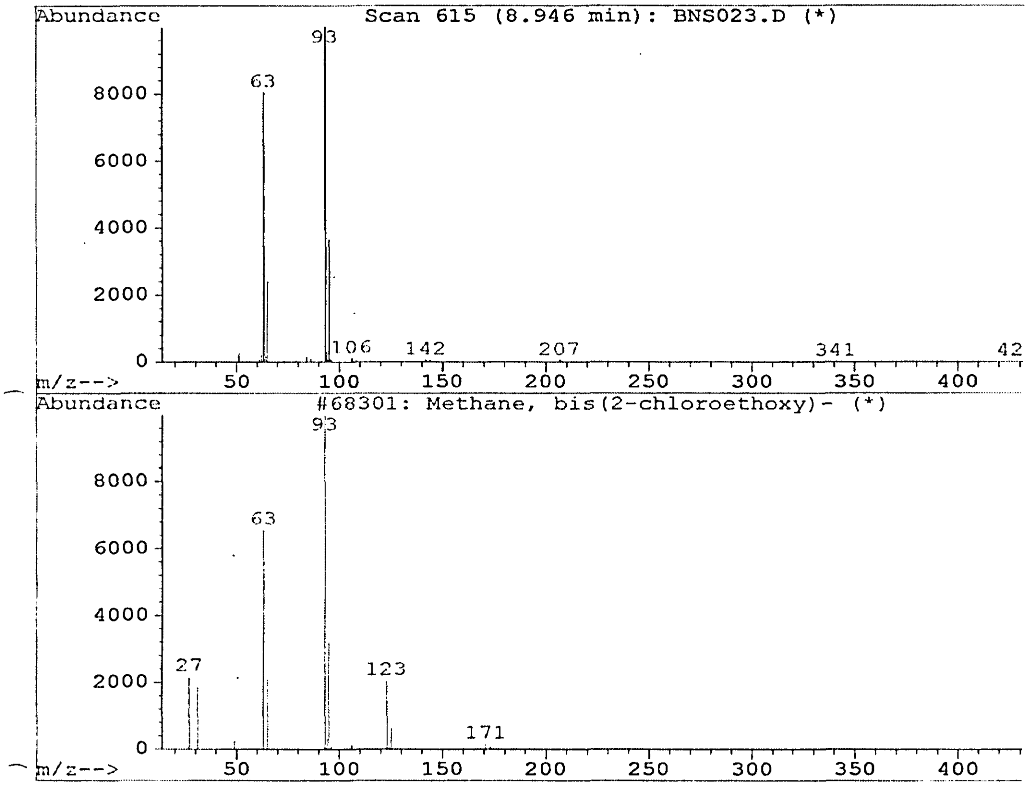
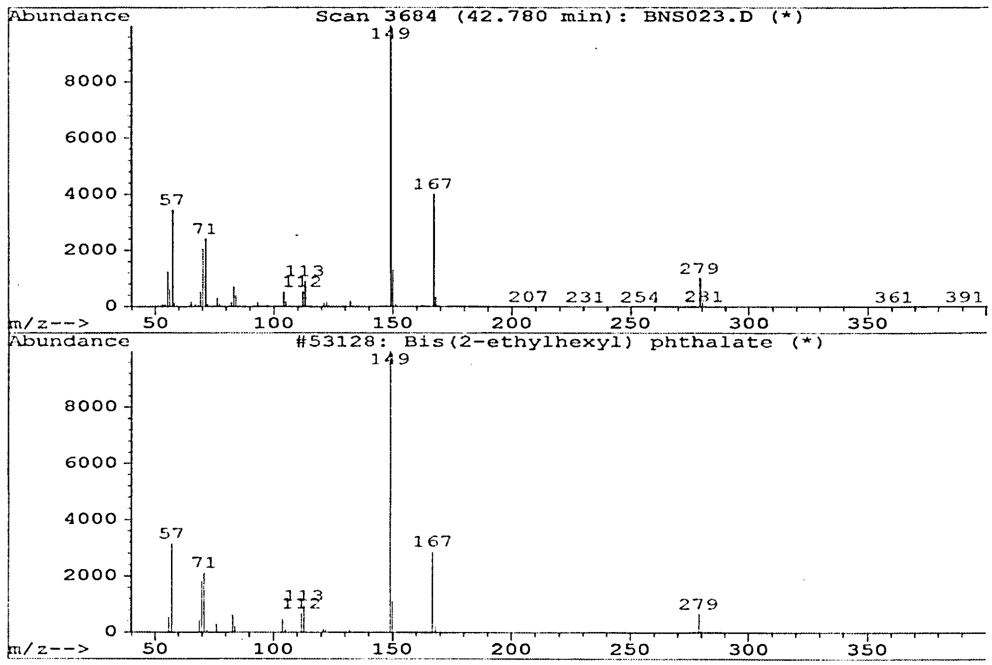


Figure 4.7 Mass spectra of benzo(ghi)perylene and bis(2 chloroethoxy) methane in standard of Base/Neutral fraction.

ID : Bis(2-ethylhexyl) phthalate



ID : Bis(2-chloroisopropyl) ether

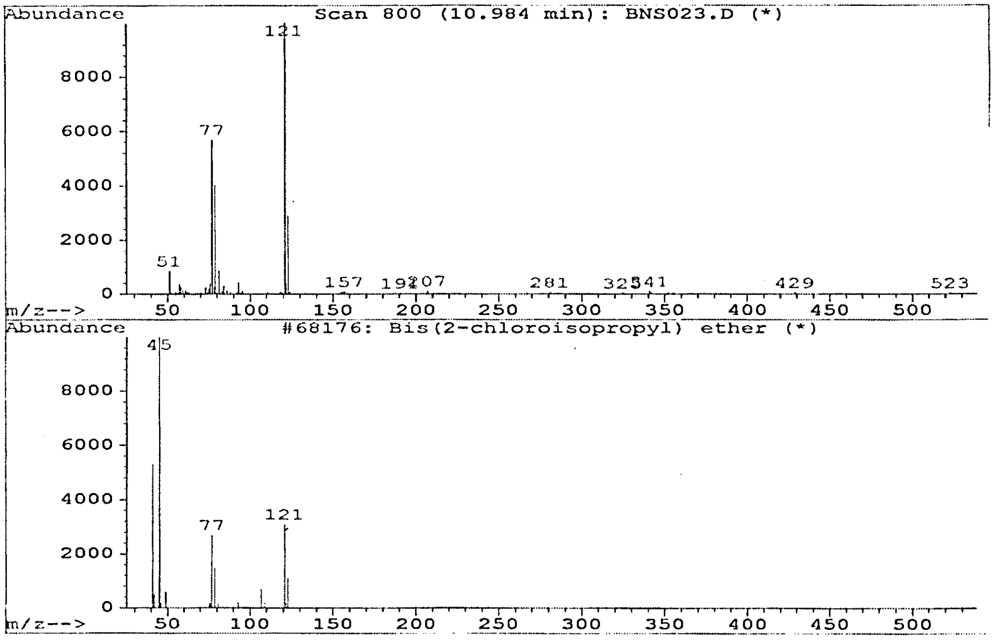


Figure4.8 Mass spectrum of bis (2-ethylhexyl) phthalate and bis (2-chloroisopropyl) ether in standard of Base/Neutral fraction.

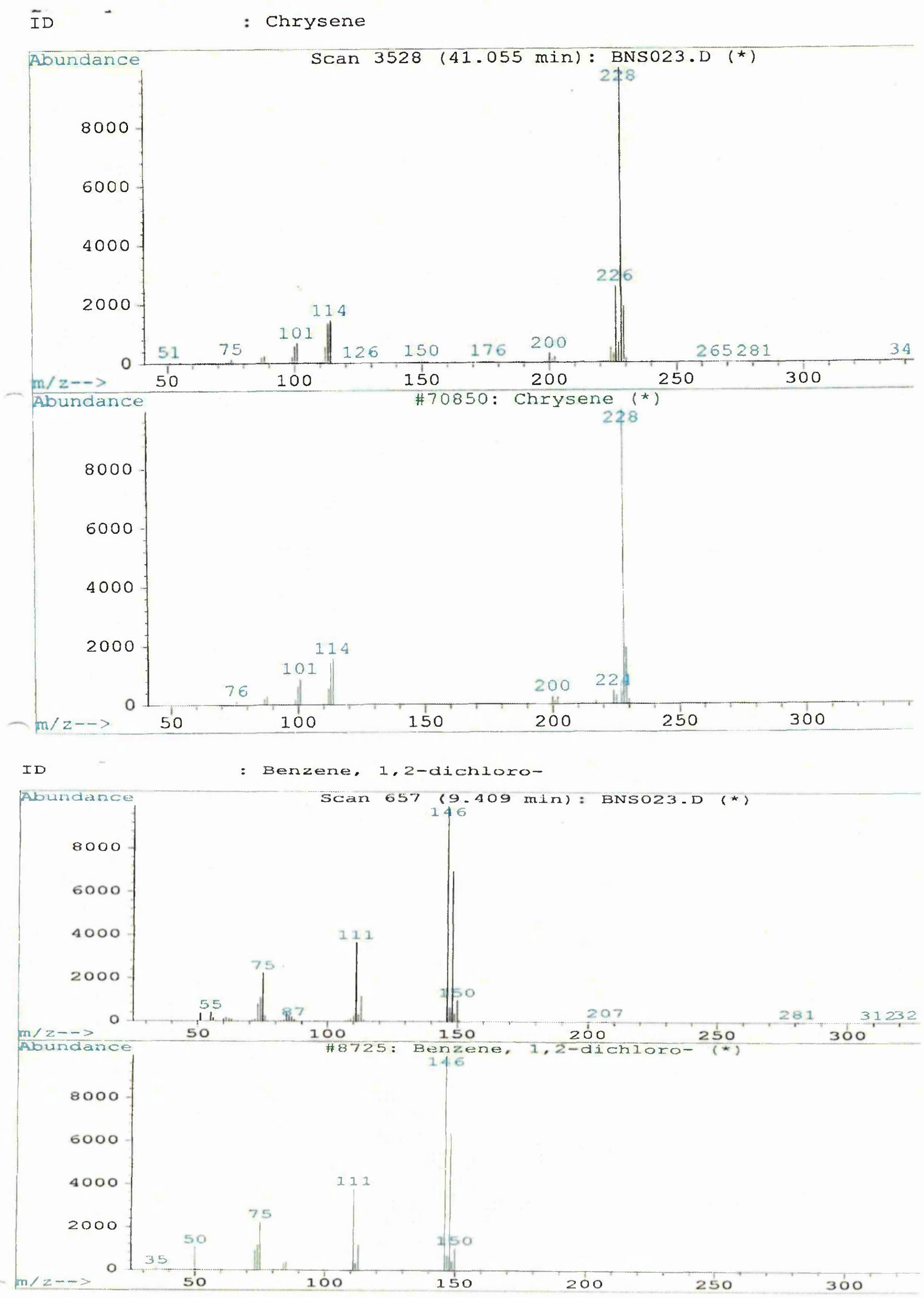
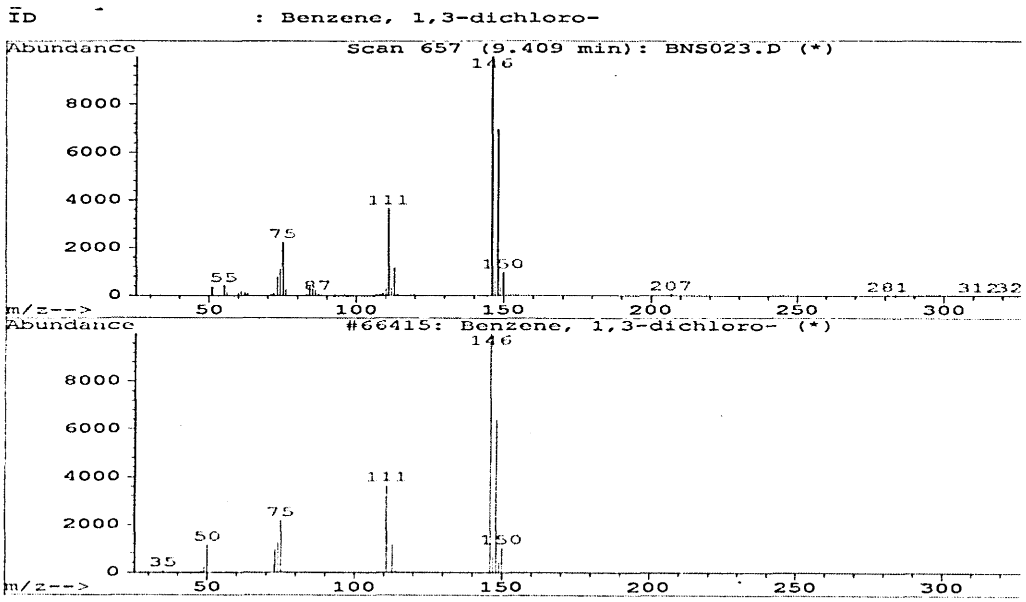


Figure 4.9 Mass spectra of chrysene and 1,2 dichlorobenzene in standard of Base/Neutral fraction.



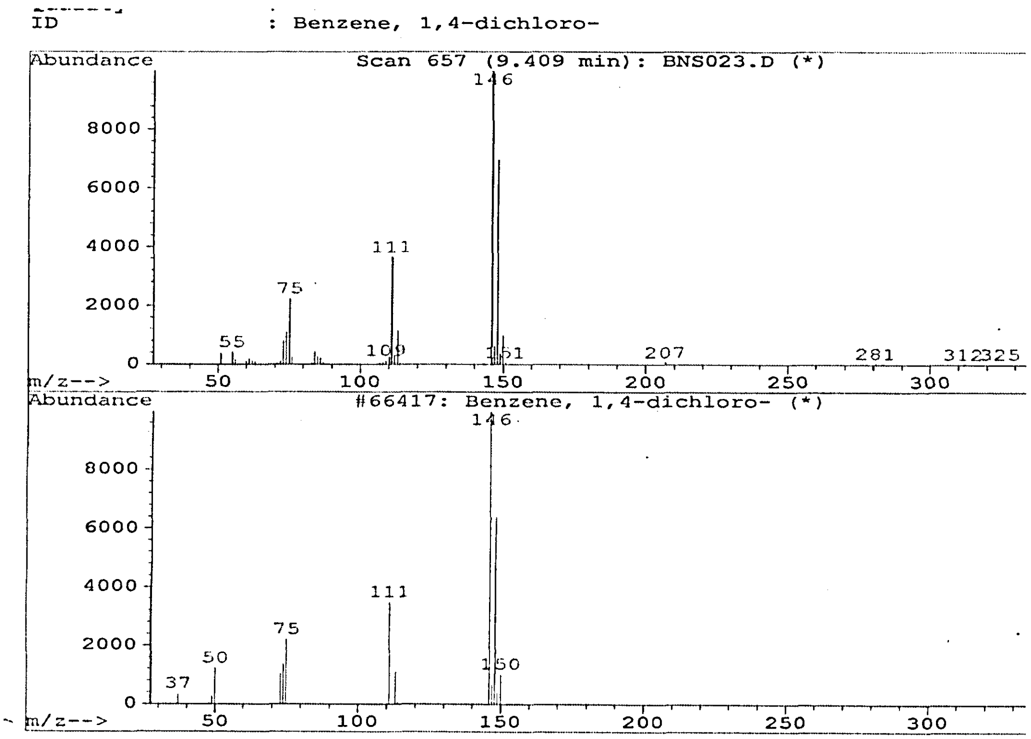


Figure 4.10 Mass spectra of 1,3-dichlorobenzene and 1,4-dichlorobenzene in standard of Base/Neutral fraction.

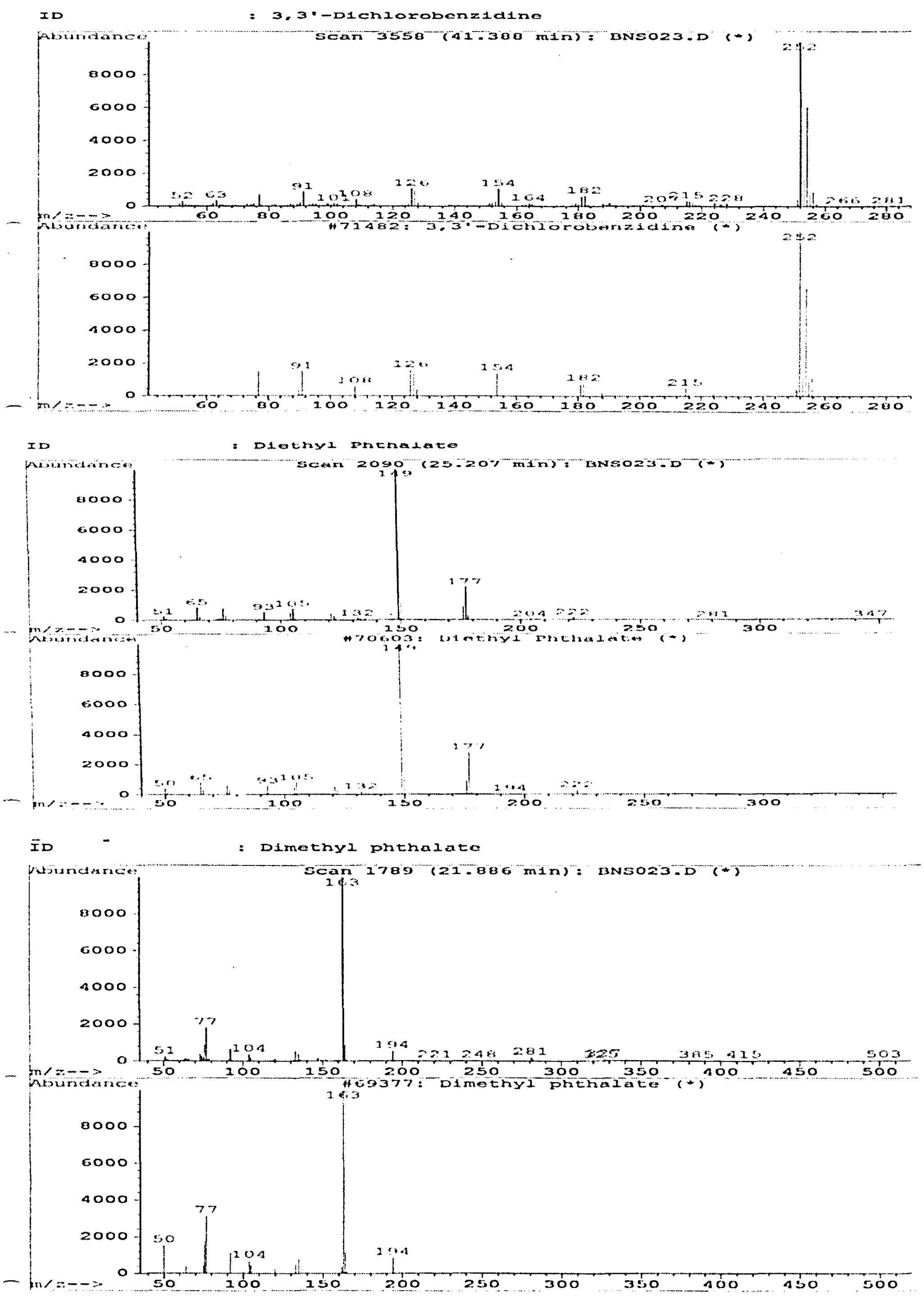


Figure 4.11 Mass spectra of 3,3'-dichlorobenzidine, diethyl phthalate and dimethyl phthalat in standard of Base/Neutral fraction.

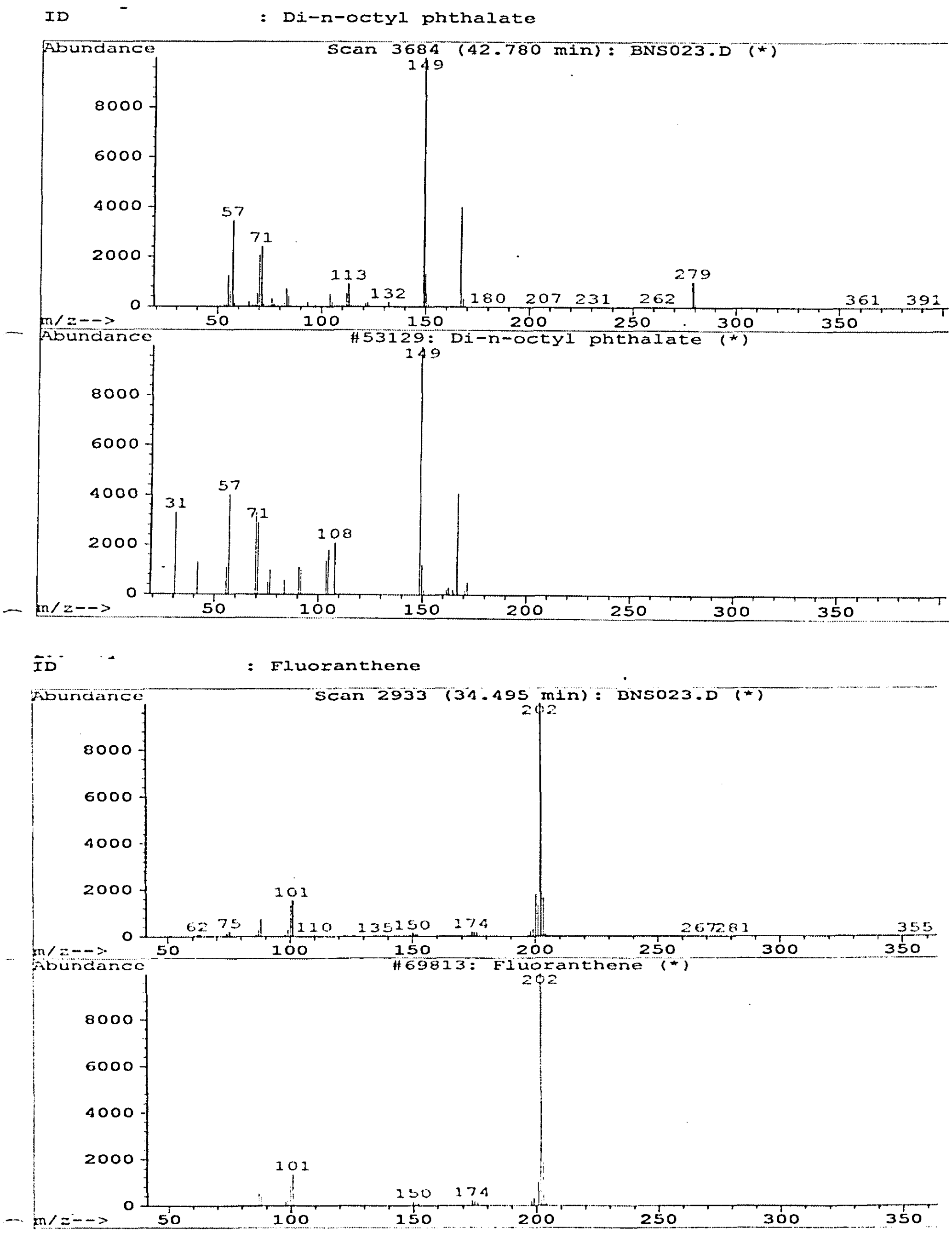


Figure 4.12 Mass spectra di-n-octylphthalate and fluoranthene in standard of Base/Neutral fraction.

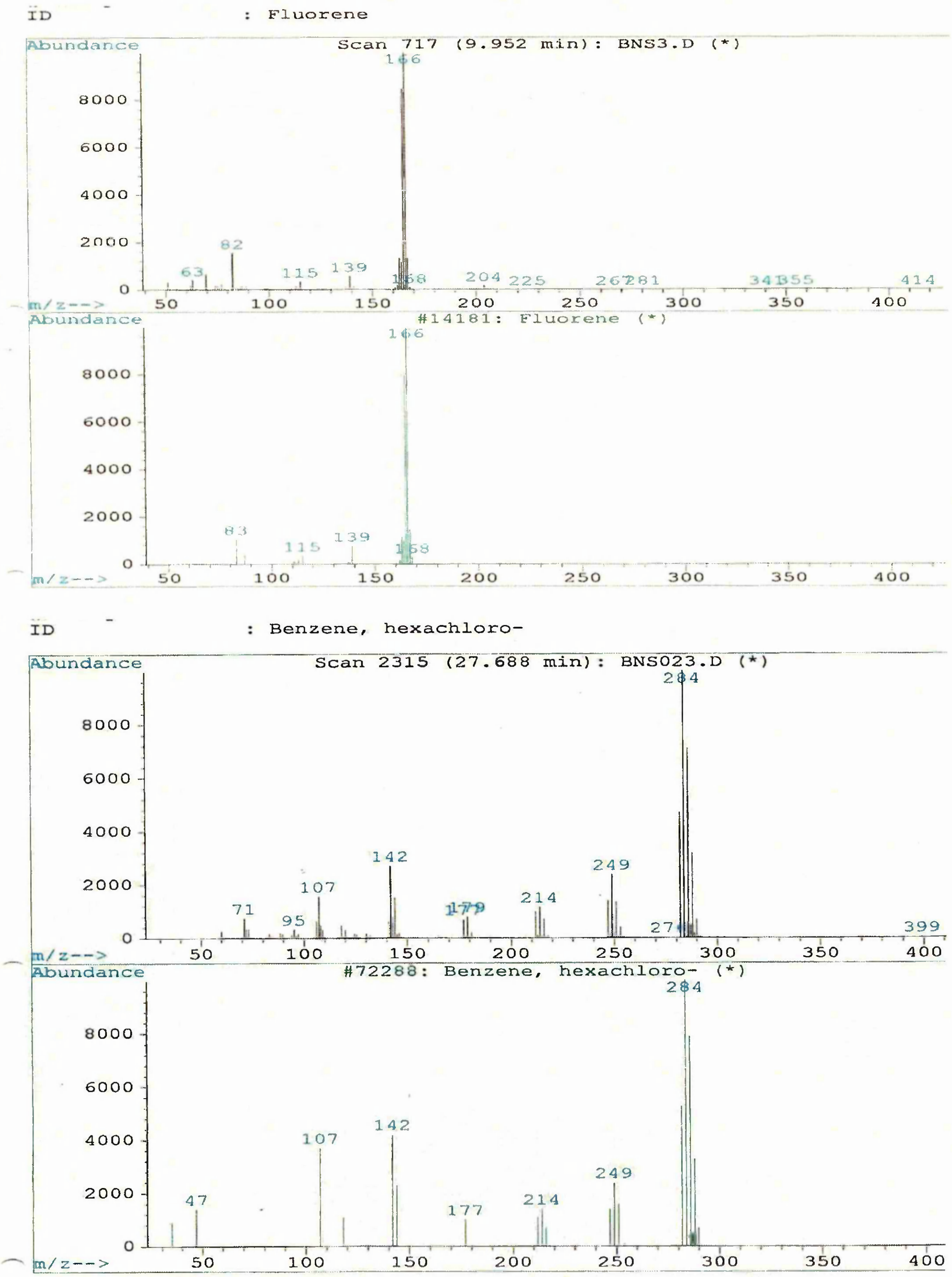
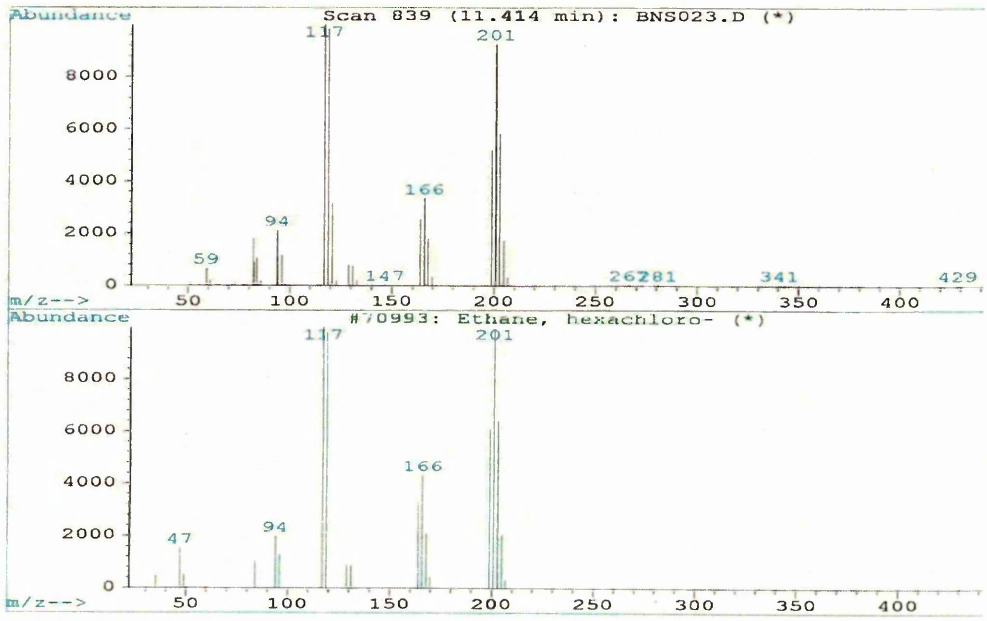


Figure 4.13 Mass spectra of fluorene and hexachlorobenzene in standard of Base/Neutral fraction.

ID : Ethane, hexachloro-



ID : Indeno[1,2,3-cd]pyrene

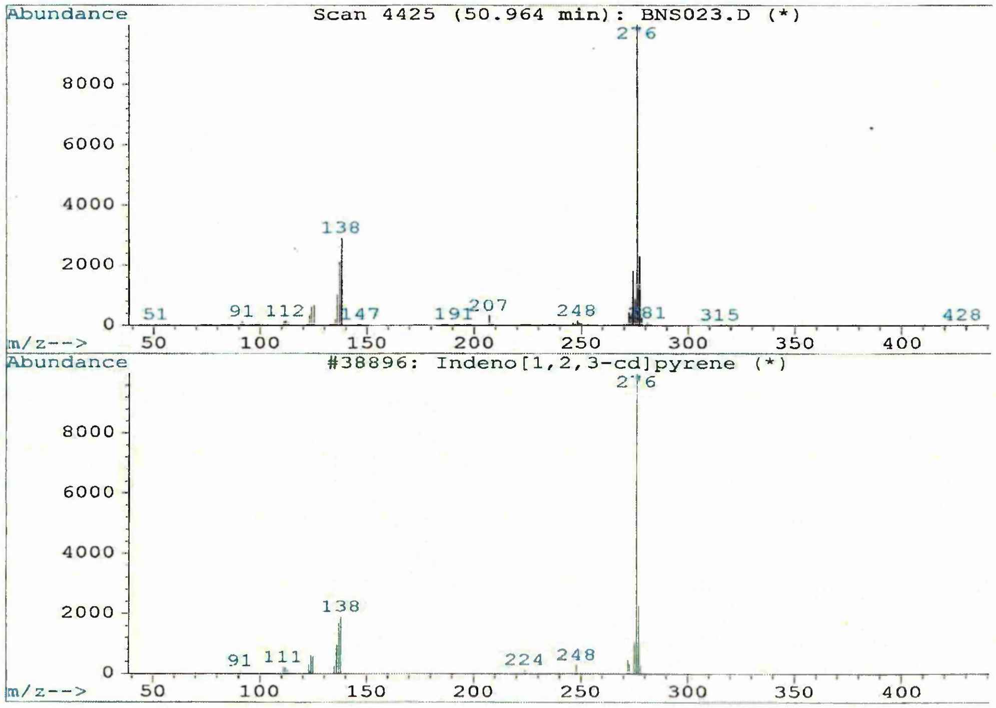
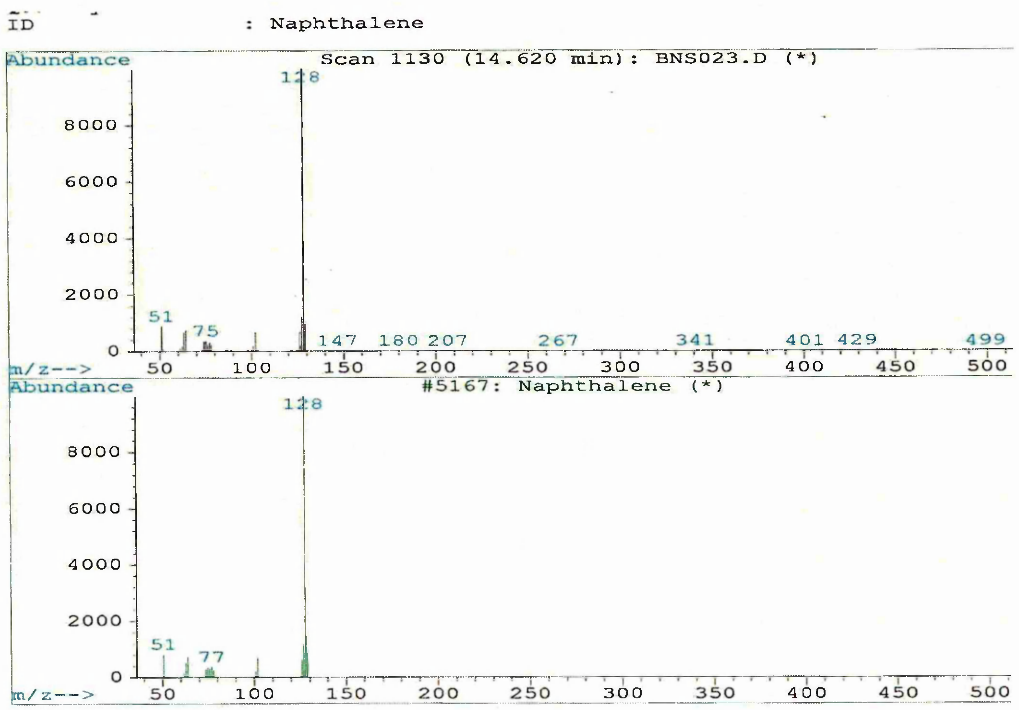


Figure 4.14 Mass spectra of hexachloroethane and indeno (1, 2, 3-cd) pyrene in standard of Base/Neutral fraction.



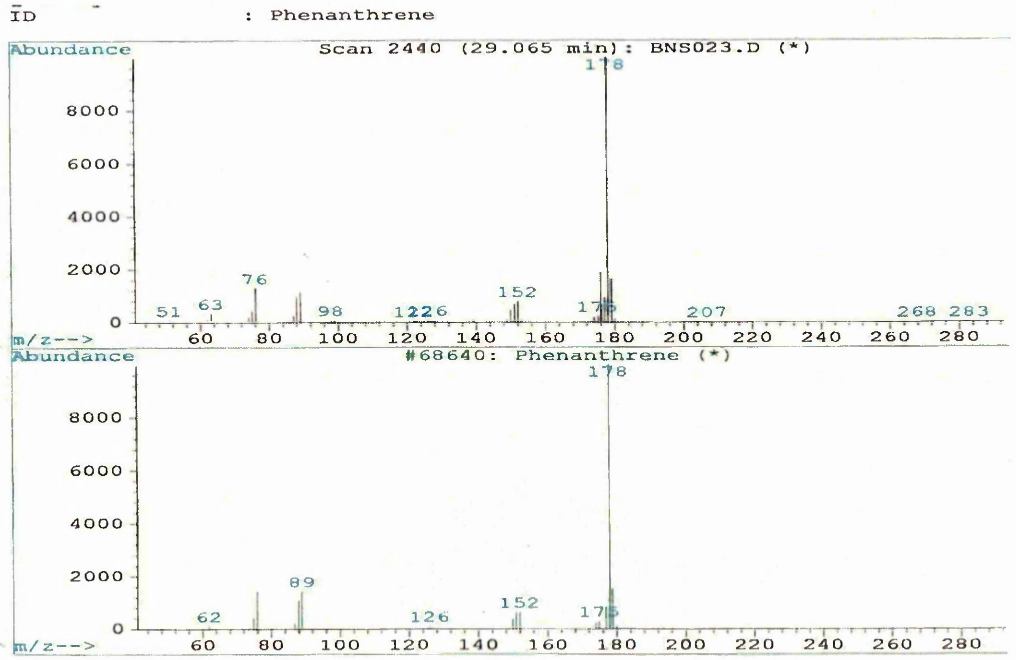
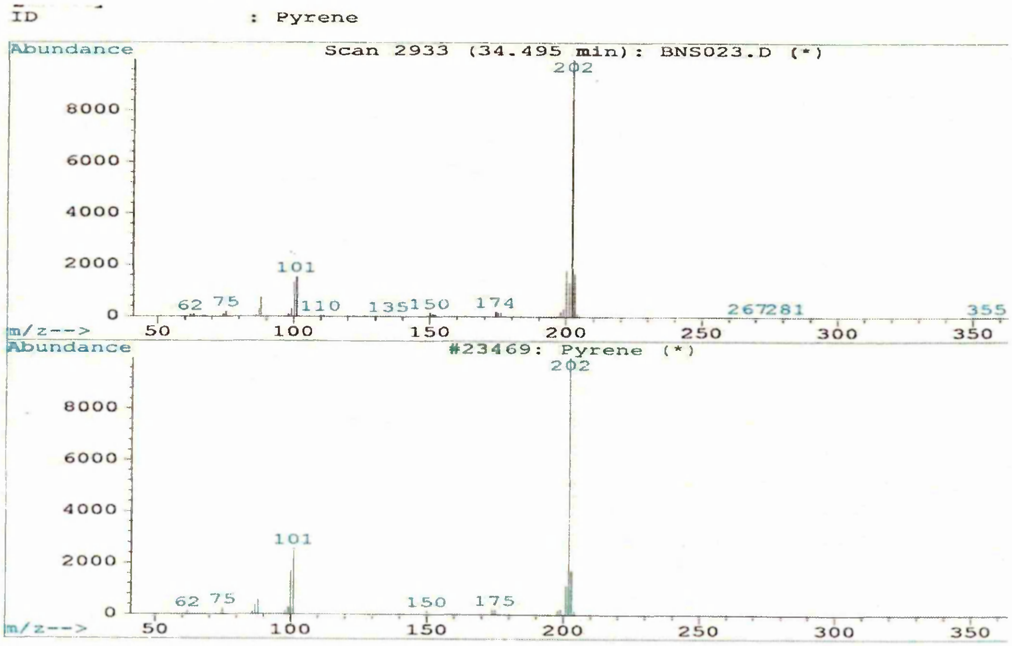


Figure 4.15 Mass spectra of naphthalene and phenanthrene in standard of Base/Neutral fraction.



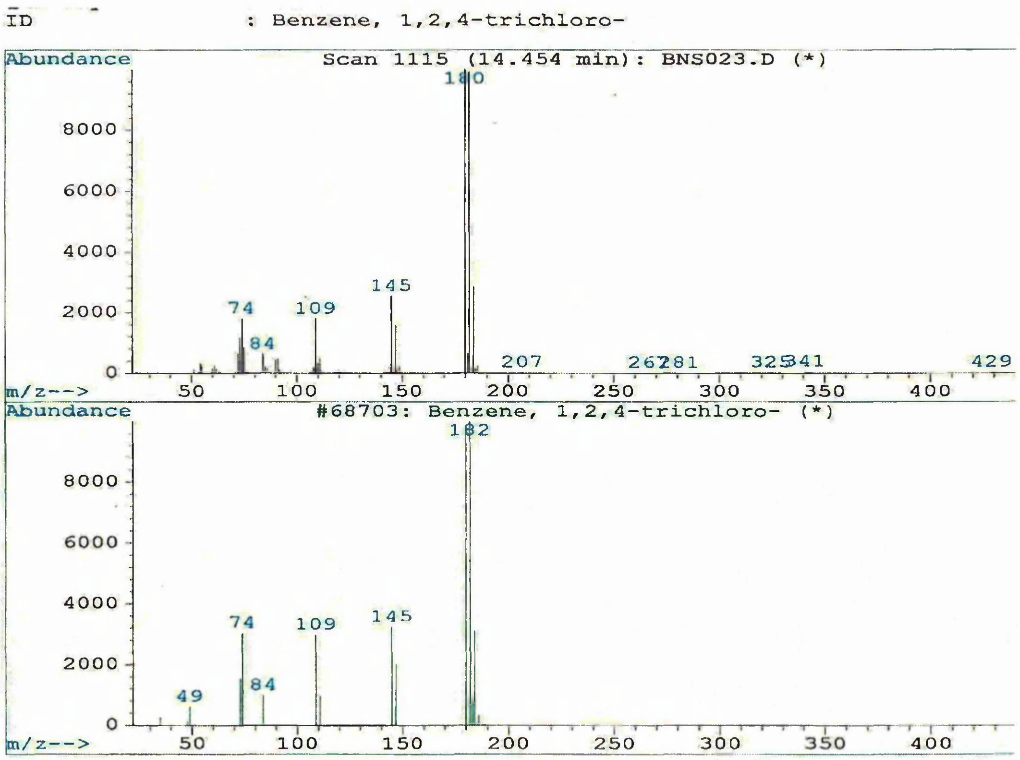


Figure 4.16 Mass spectra pyrene and 1,2,4-trichlorobenzene in standard of Base/Neutral fraction.

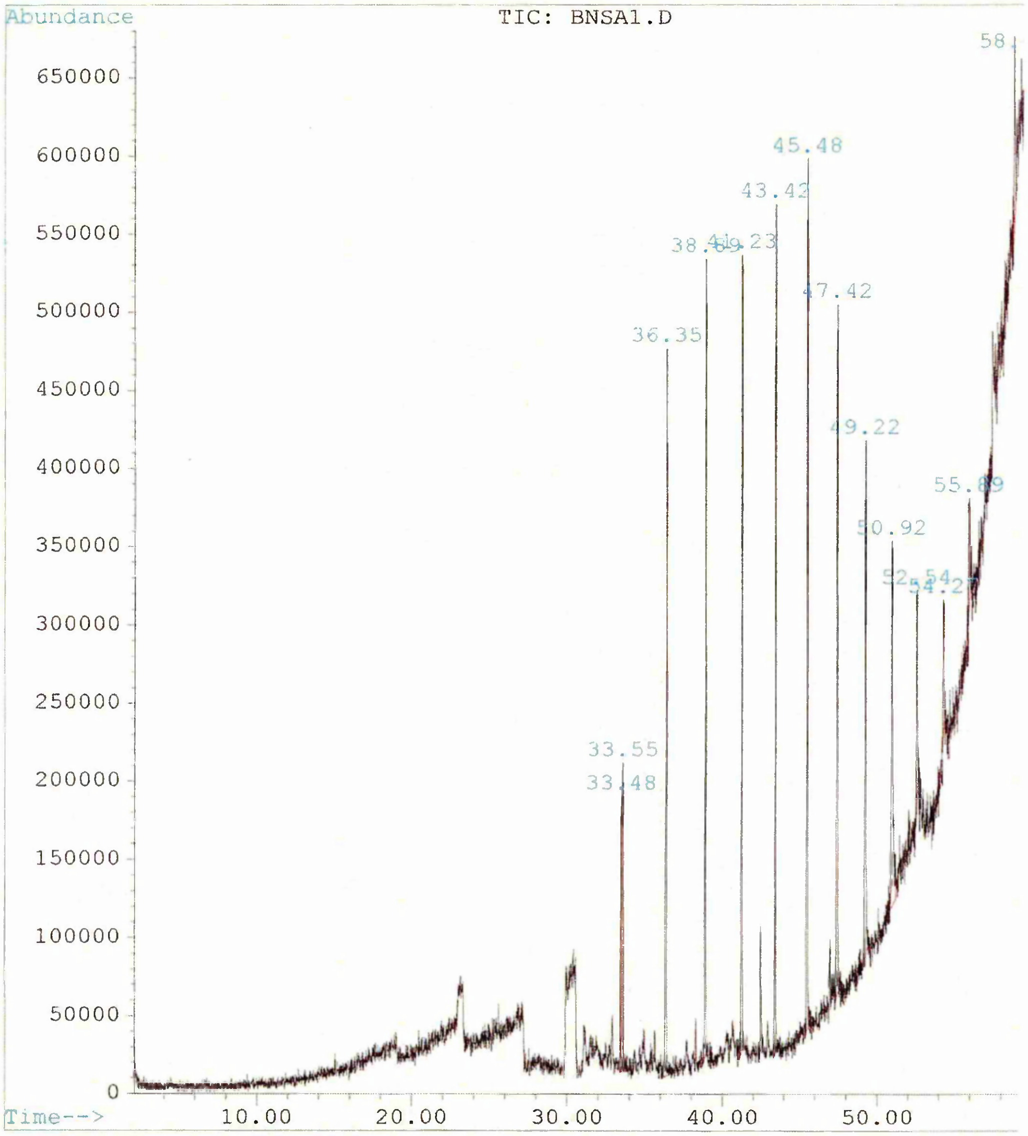


Figure 4.17 Total ion chromatogram (TIC) of the Base/Neutral fraction extracted from sample 1

Selected- ion monitoring(SIM) mode

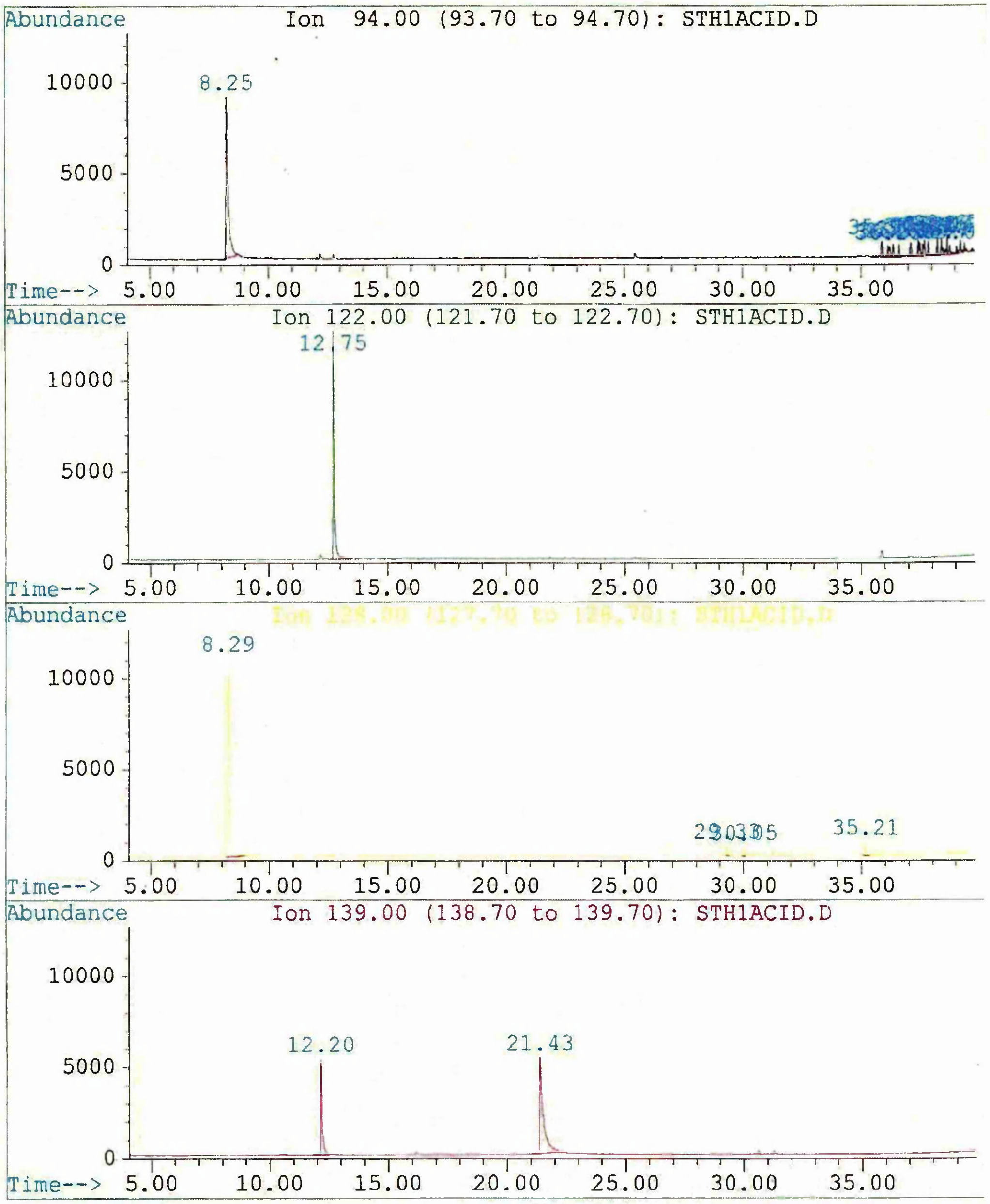


Figure 4.18 SIM chromatograms of ions m/z 94 (phenol), 122 (2,4-dimethylphenol), 128 (2-chlorophenol), 139 (4-nitrophenol) in standard (100:10 ng/ ml) of the acid fraction.

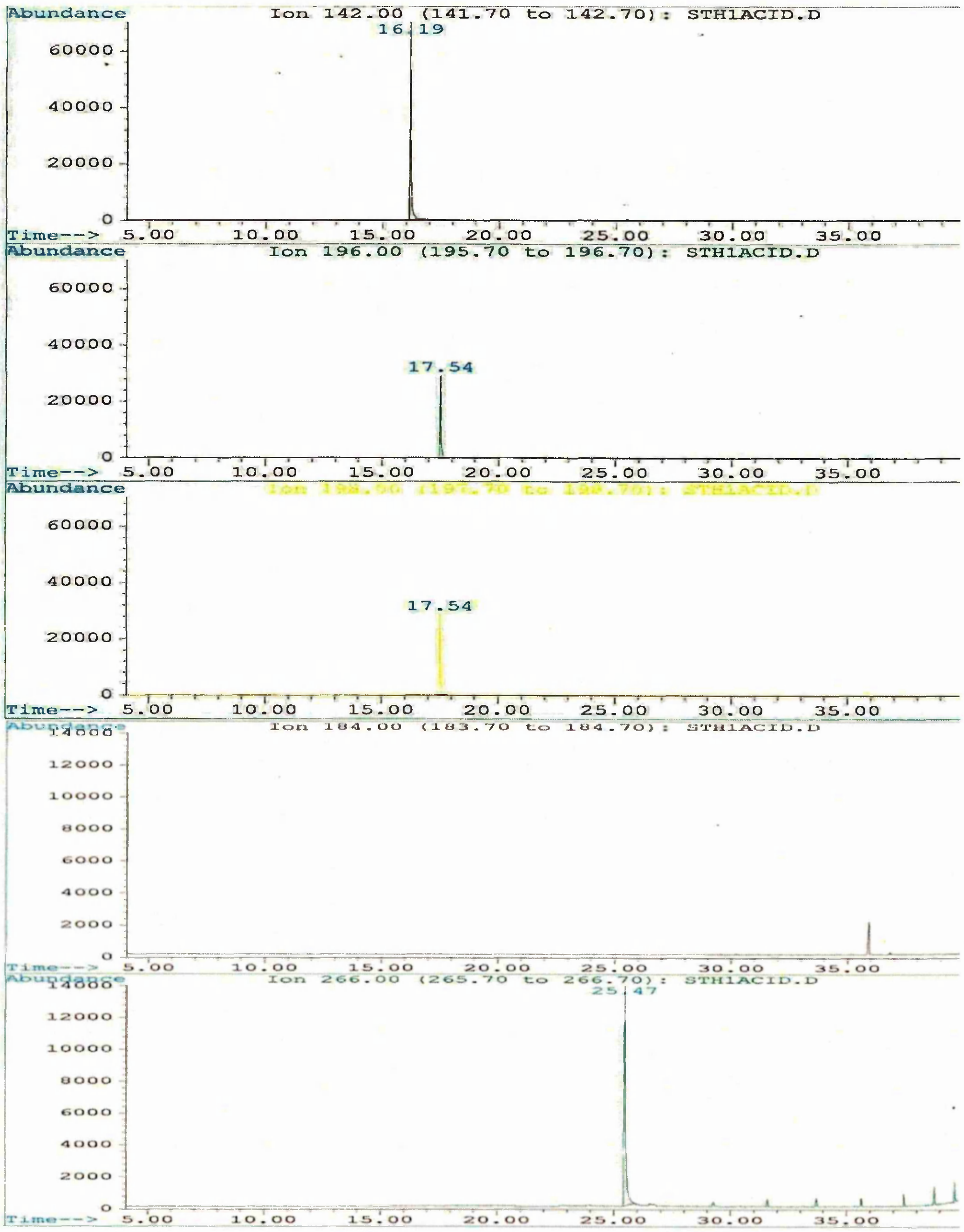


Figure 4.19 SIM chromatograms of selected ions m/z 142 (4-chloro-3methylphenol), 196 (2, 4, 6-trichlorophenol), 198 (2-methyl-4, 6-dinitrophenol), 184 (2, 4-dinitrophenol), 266 (pentachlorophenol) in standard (100:10ng/ ml) of the acid fraction.

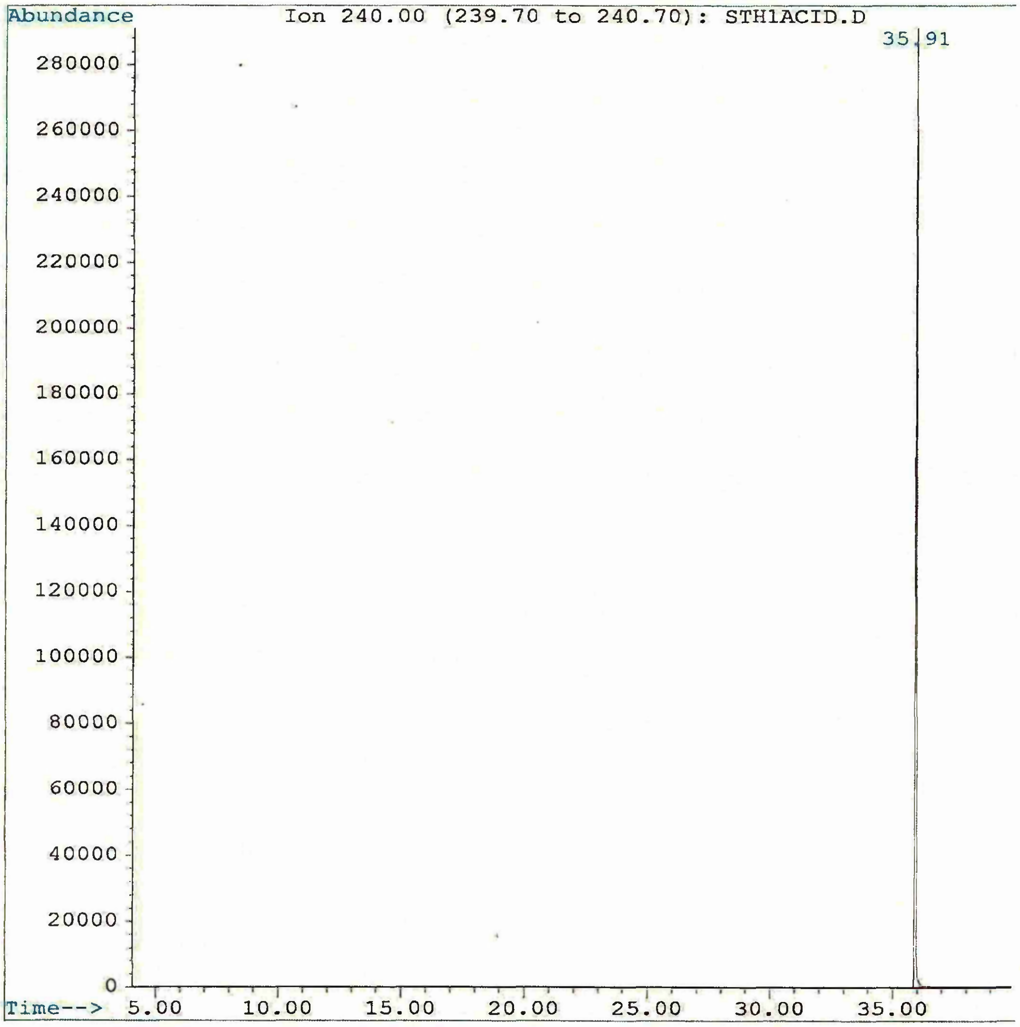


Figure 4.20 SIM chromatogram of selected ion m/z 240 (chrysene-d_{12}) in standard (100:10 ng/ ml) of the acid fraction.

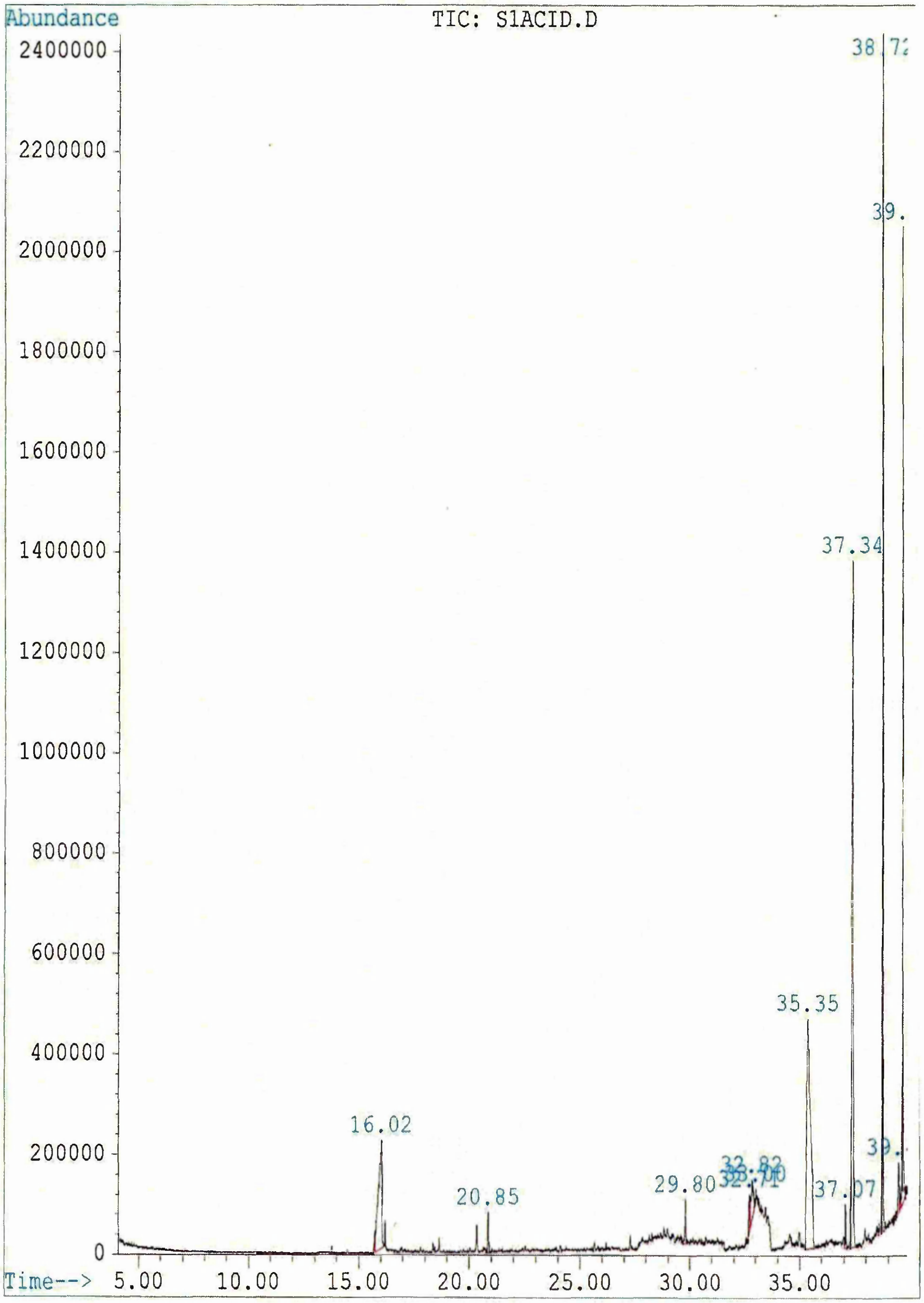


Figure 4.21 Typical chromatogram (TIC) of the acid fraction extracted from sample1

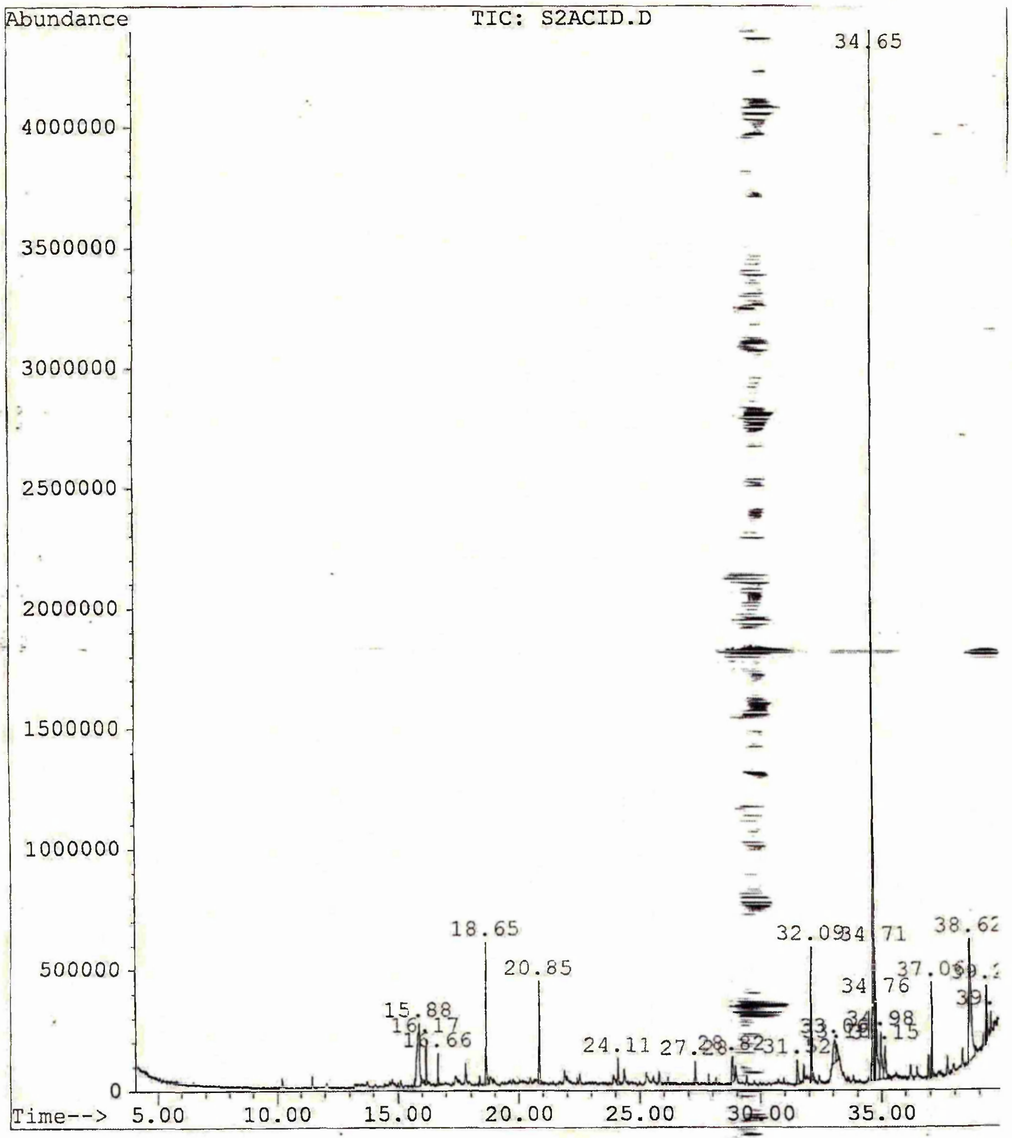


Figure 4.22 Typical chromatogram (TIC) of the acid fraction extracted from sample2

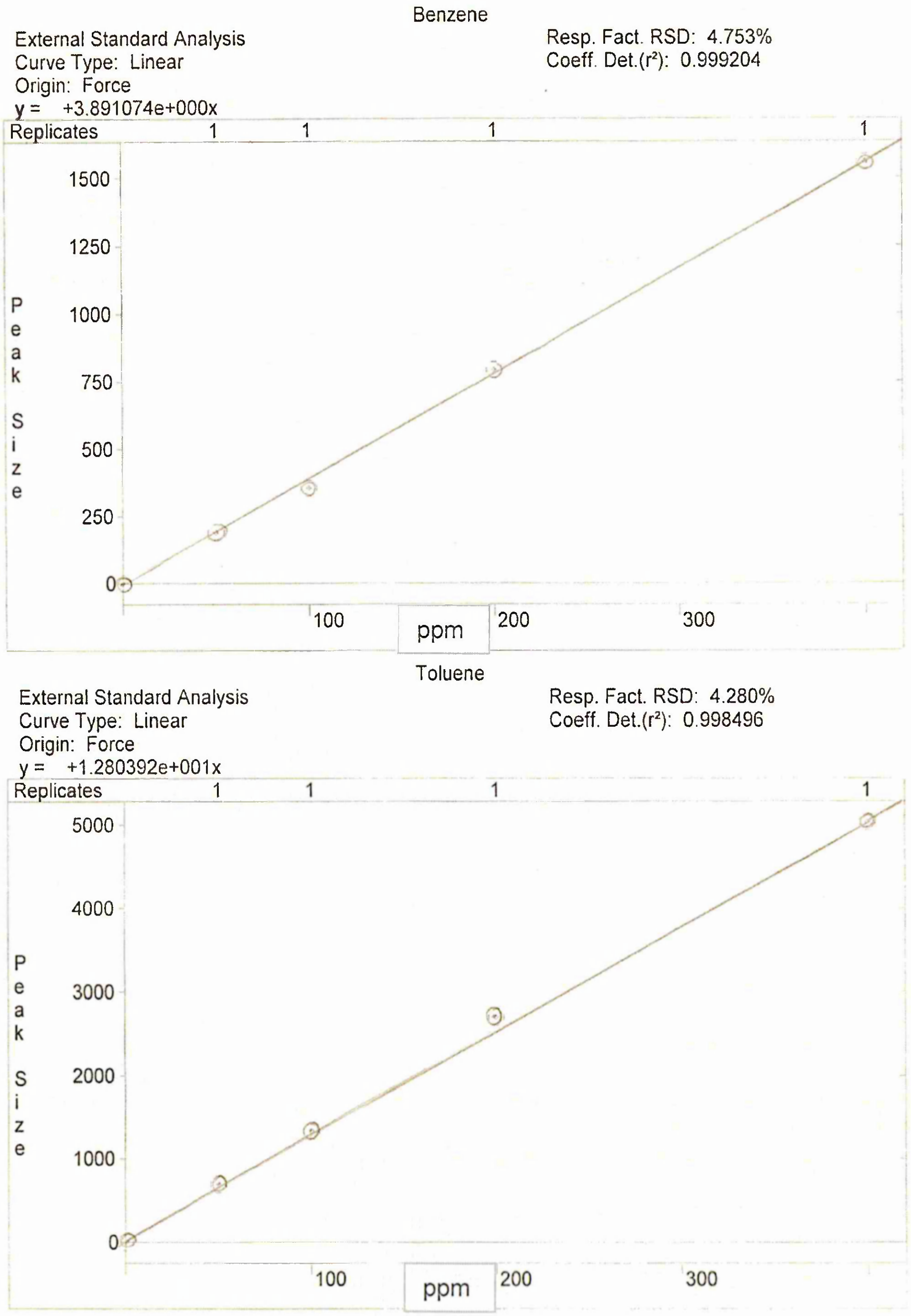


Figure 4.23 Calibration graph of benzene and toluene standard solution

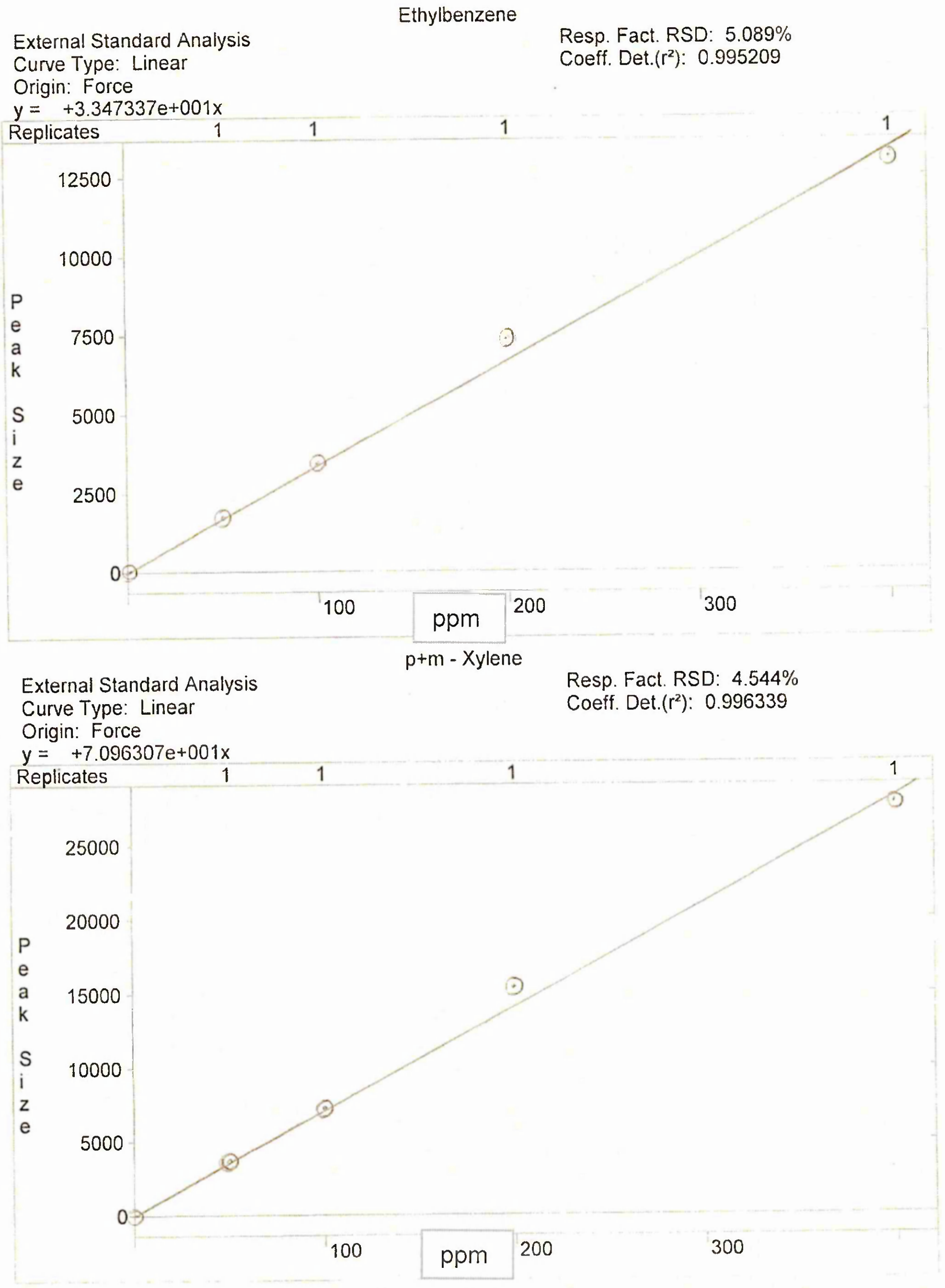


Figure 4.24 Calibration graph of ethylbenzene and p+m- xylene standard solution

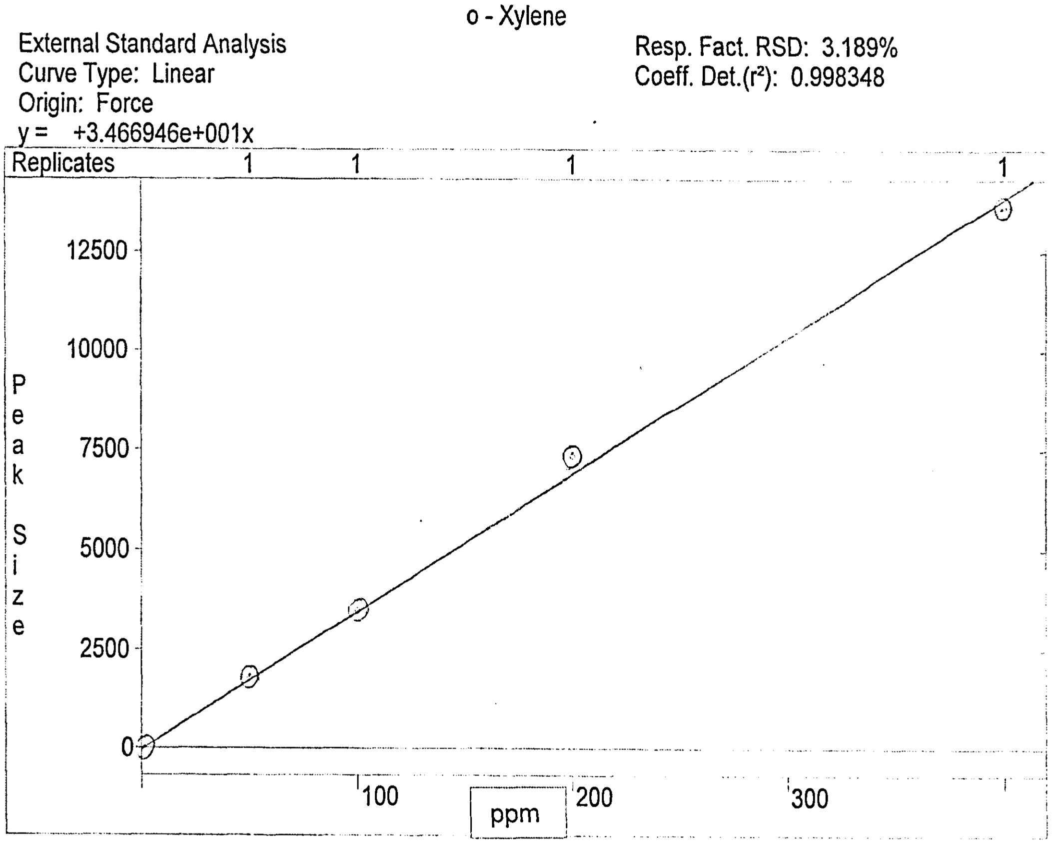


Figure 4.25 Calibration graph of o- xylene standard solution

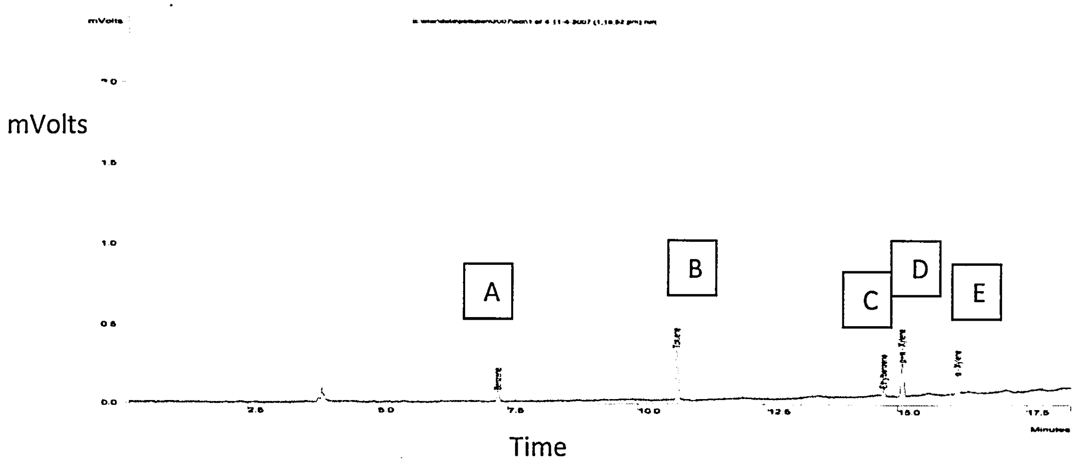


Figure 4.26 Chromatogram of A (benzene) , B (toluene), C (ethylbenzene), D (p+m -xylene) and E (o- xylene) in sample 1

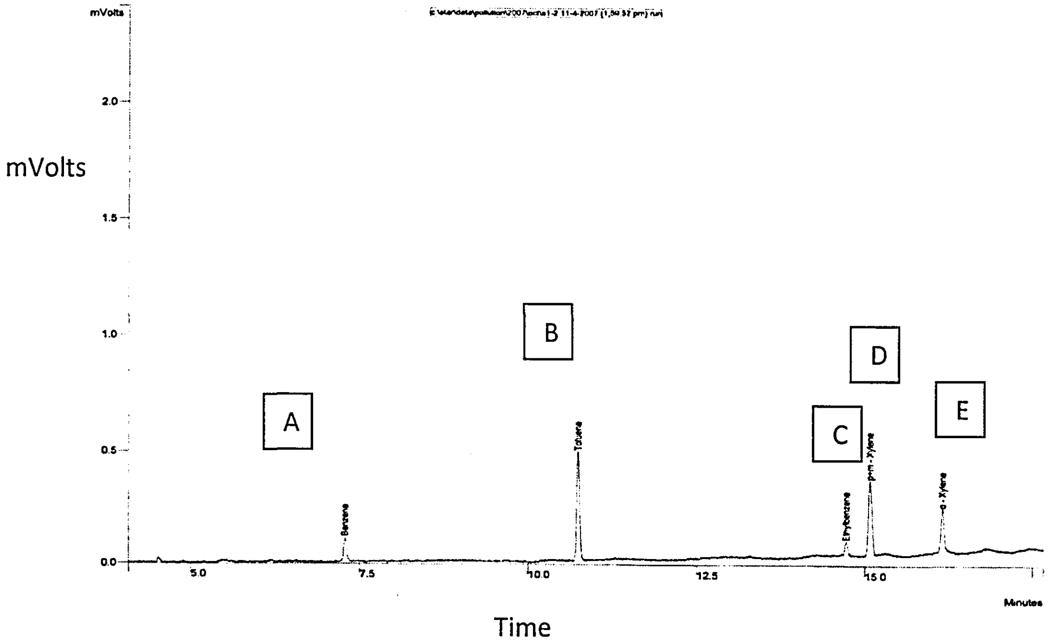


Figure 4.27 Chromatogram of A (benzene) , B (toluene), C (ethylbenzene), D (p+m -xylene) and E (o- xylene) in sample 2

B

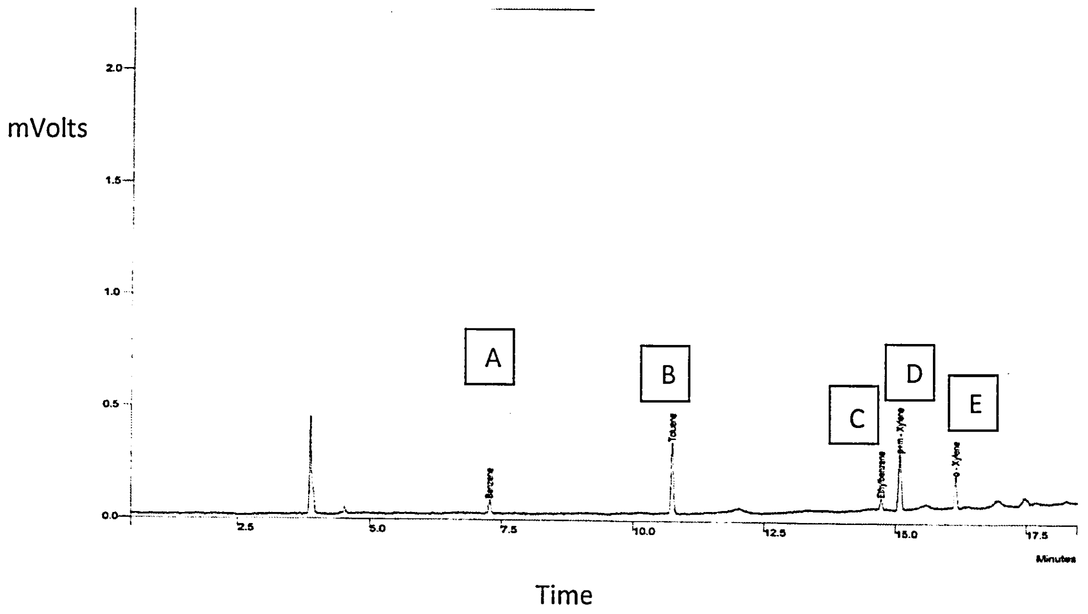


Figure 4.28 Chromatogram of A (benzene) , B (toluene), C (ethylbenzene), D (p+m -xylene) and E (o- xylene) in sample 3

C

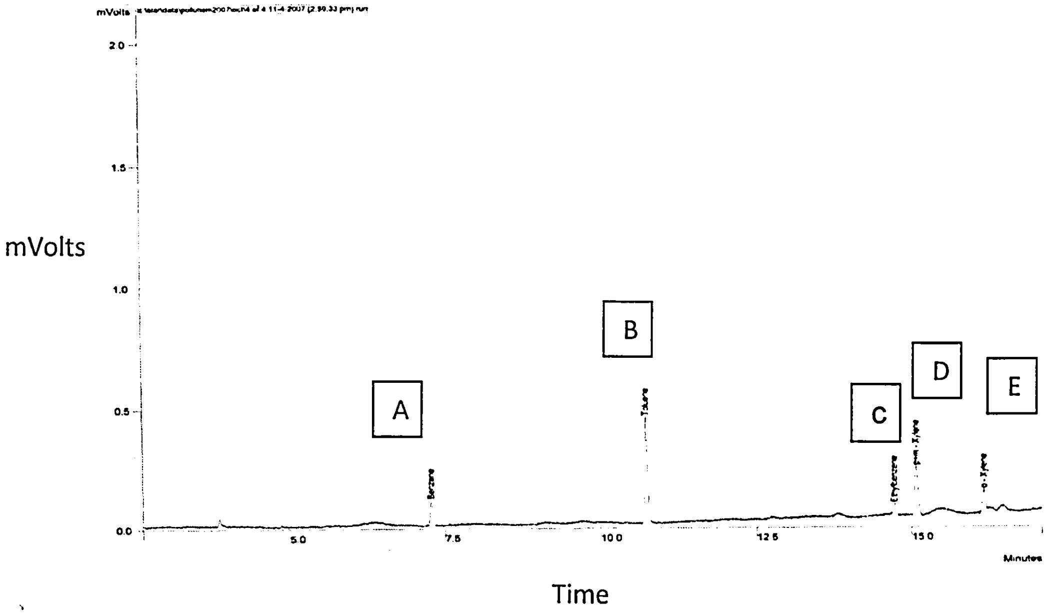


Figure 4.29: Chromatogram of A (benzene) , B (toluene), C (ethylbenzene), D (p+m -xylene) and E (o- xylene) in sample 4

Table 4. 13 Concentration and peak area of mass ions in standard calibration for PAH analysis.

Molecular mass Concentration mg/l	0	2	5	10	15	20
Peak area 152	0	800444	3468530	7661525	13171571	16743648
Peak area 154	0	745856	2430614	4413229	7177114	9624310
Peak area 166	0	250249	1422897	2804358	4860256	7272935
Peak area 178	0	860470	2351569	4522969	7478350	10093396
Peak area 202	0	760546	2573966	5687654	10736535	15056393
Peak area 228	0	475262	2097287	3679246	5972142	8220989
Peak area 252	0	910112	2163323	4101574	6327108	8207213
Peak area 276	0	597473	1797188	4507237	6922617	10047242
Peak area 278	0	267737	820463	1860210	2949188	405455

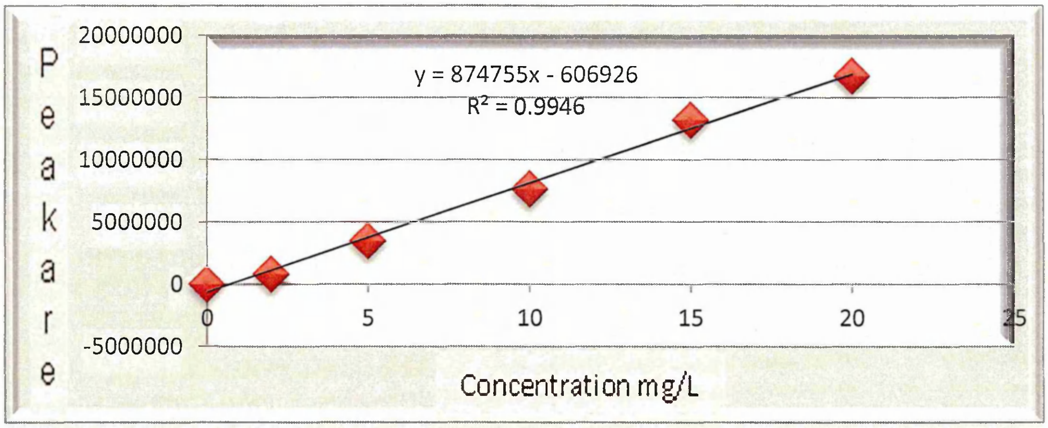


Figure 4.30: Calibration graph of ion m/z 152 acenaphthylene in standard solution

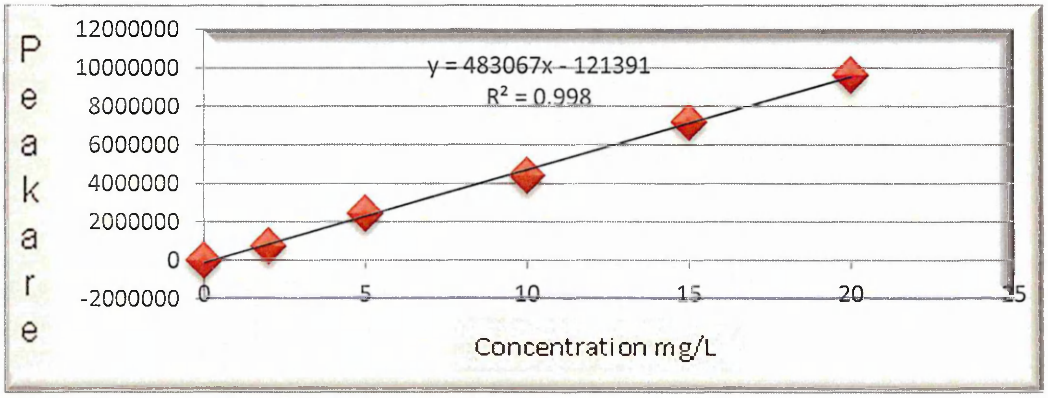


Figure 4.31: Calibration graph of ion m/z 154 acenaphthene in standard solution

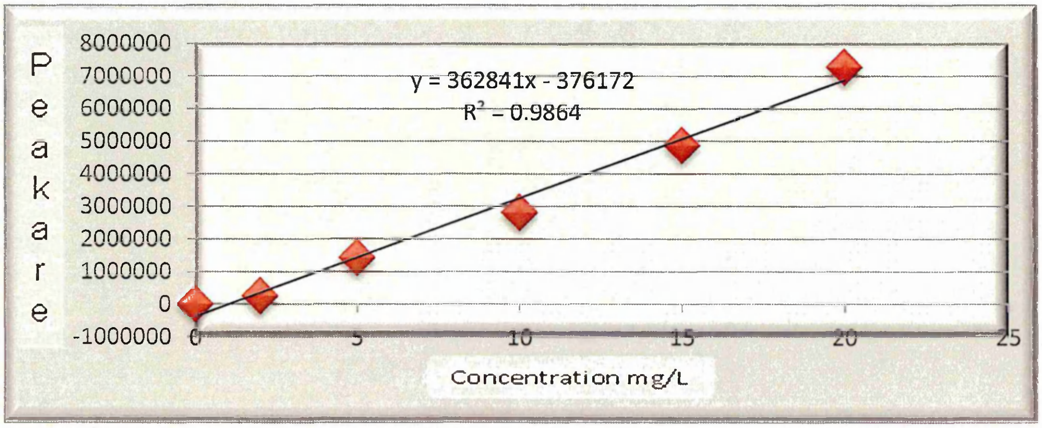


Figure 4.32: Calibration Graph of ion m/z 166 fluorene in standard solution

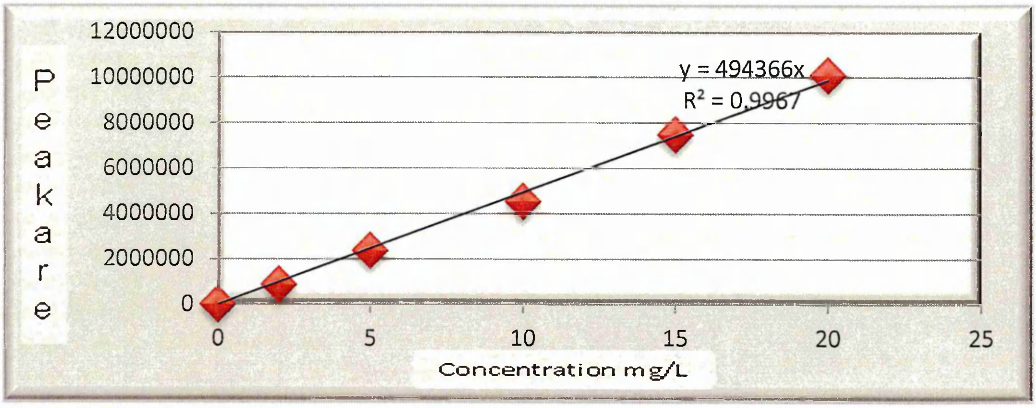


Figure 4.33: Calibration graph of ion m/z 178 phenanthrene in standard solution

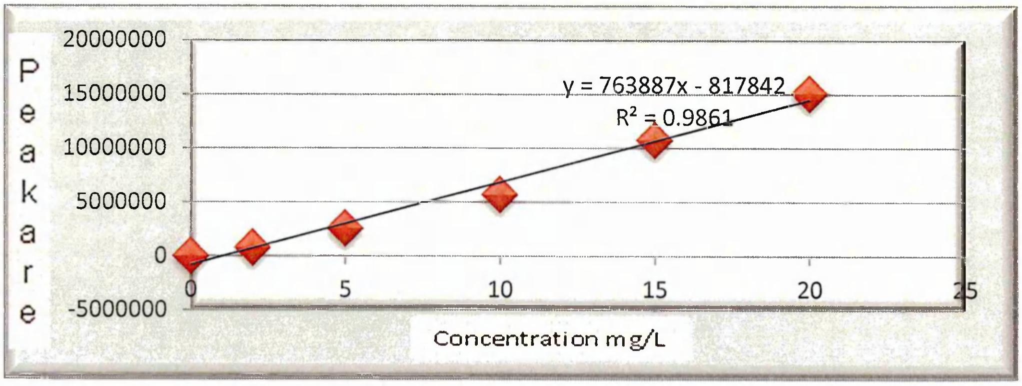


Figure 4.34: Calibration graph of m/z 202 fluoranthene and pyrene in standard solution

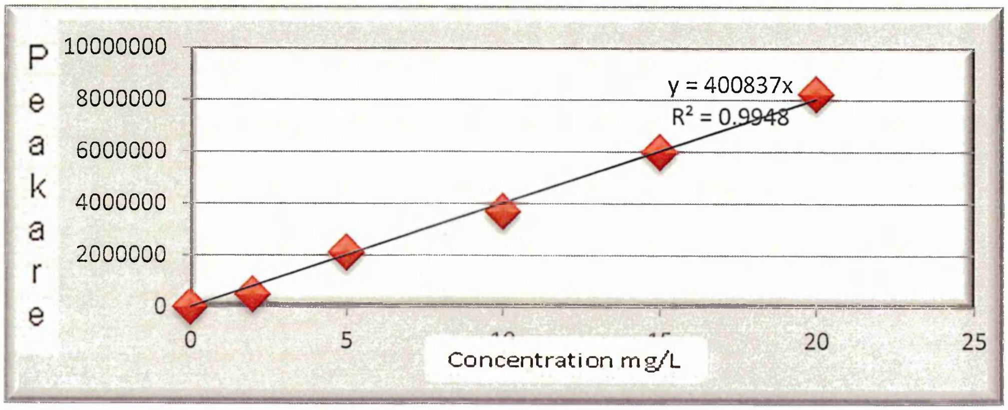


Figure 4.35: Calibration graph of ion m/z 228 benzo(a)anthracene and chrysene in standard solution

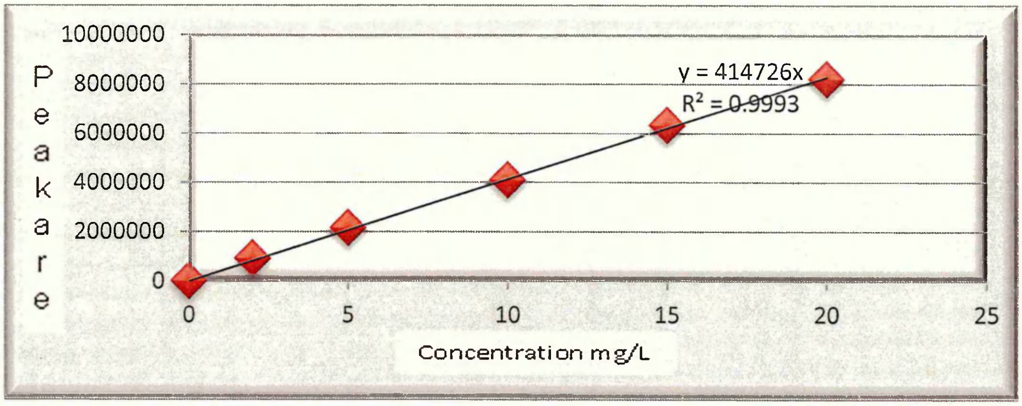


Figure 4.36: Calibration graph of ion m/z 252 benzo(b)fluoranthene and benzo(a)pyrene in standard solution

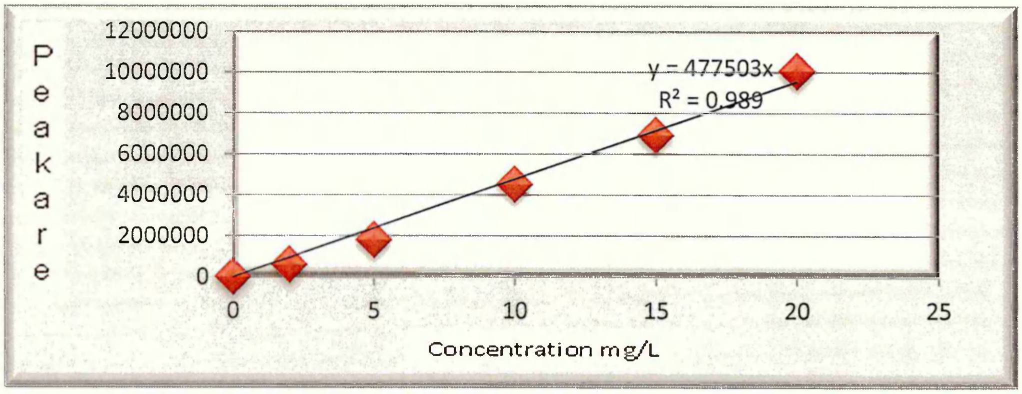


Figure 4.37: Calibration graph of ion m/z 276 indeno {1,2,3- cd)pyrene,

benzo(ghi)perylene and anthatherne in standard solution

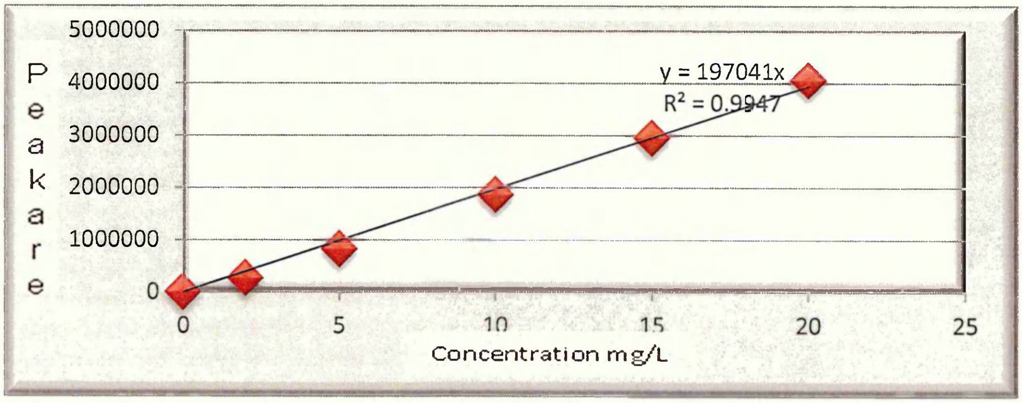


Figure 4.38: Calibration graph of ion m/z 278 dibenzo(a,h)anthracene in standard solution

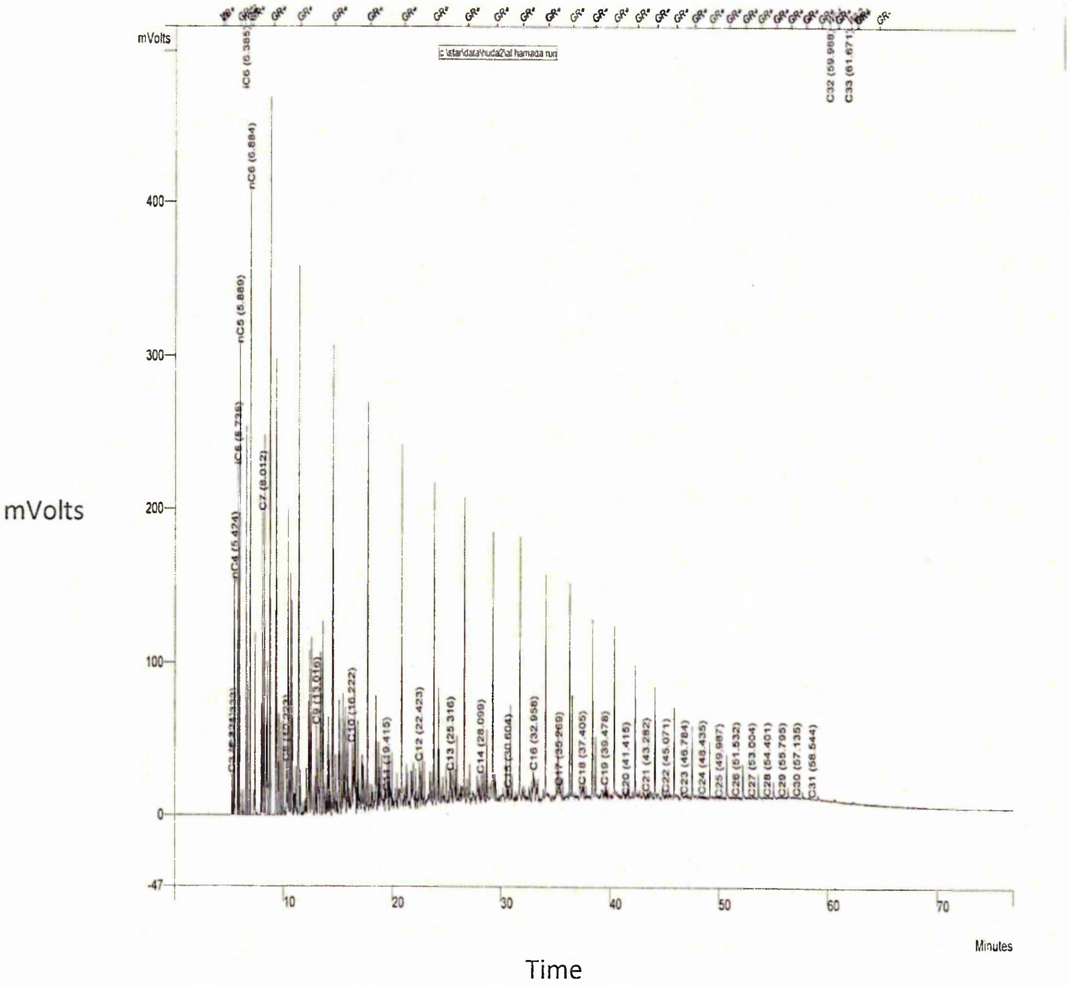


Figure 4.39 Chromatogram of carbon distribution of the crude oil from Al Hamada oilfield

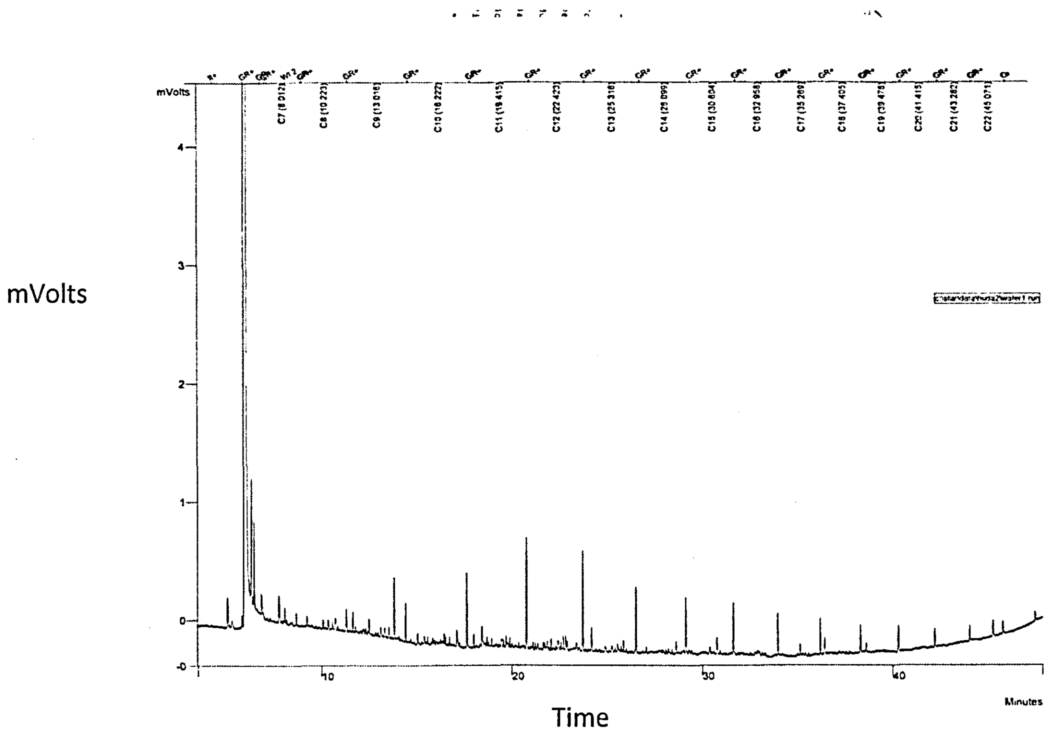


Figure4.40 Chromatogram of carbon distribution of the oil extracted from the sample 1

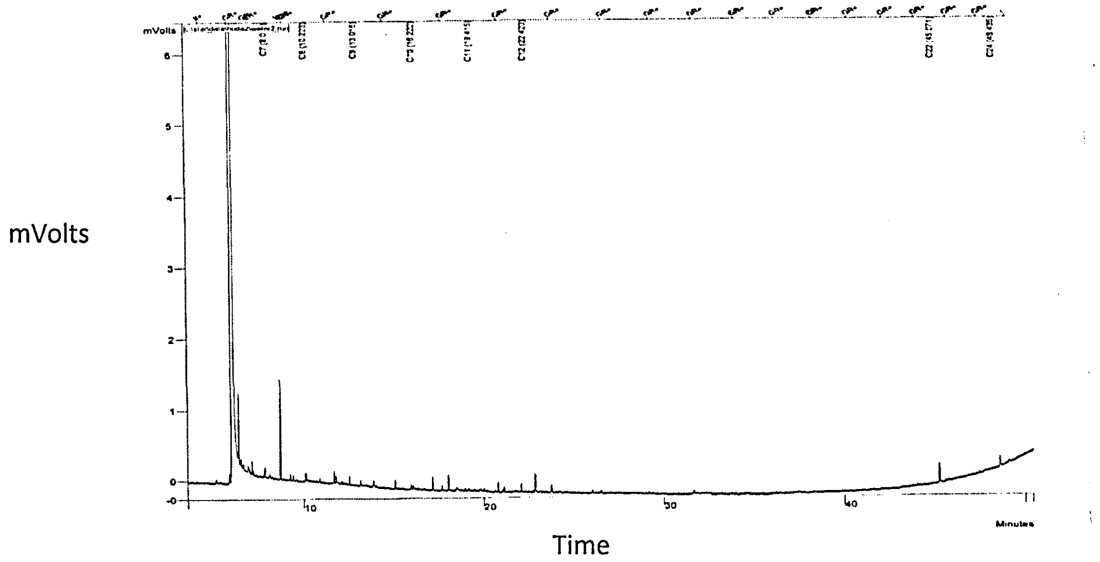


Figure 4.41 Chromatogram of carbon distribution of the oil extracted from the sample 2

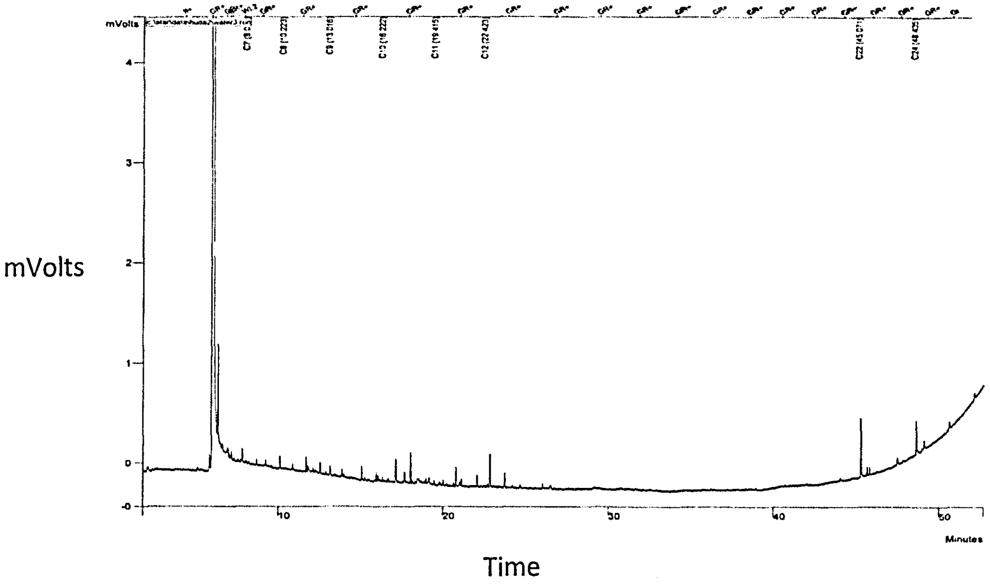


Figure4.42 Chromatogram of carbon distribution of the oil extracted from the sample 3

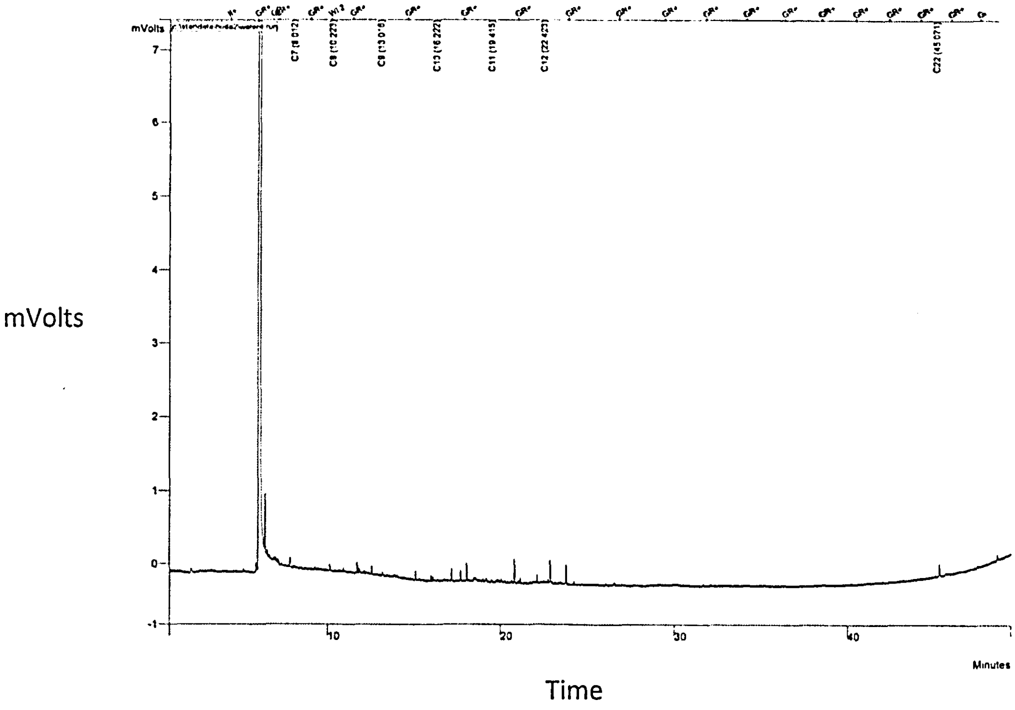
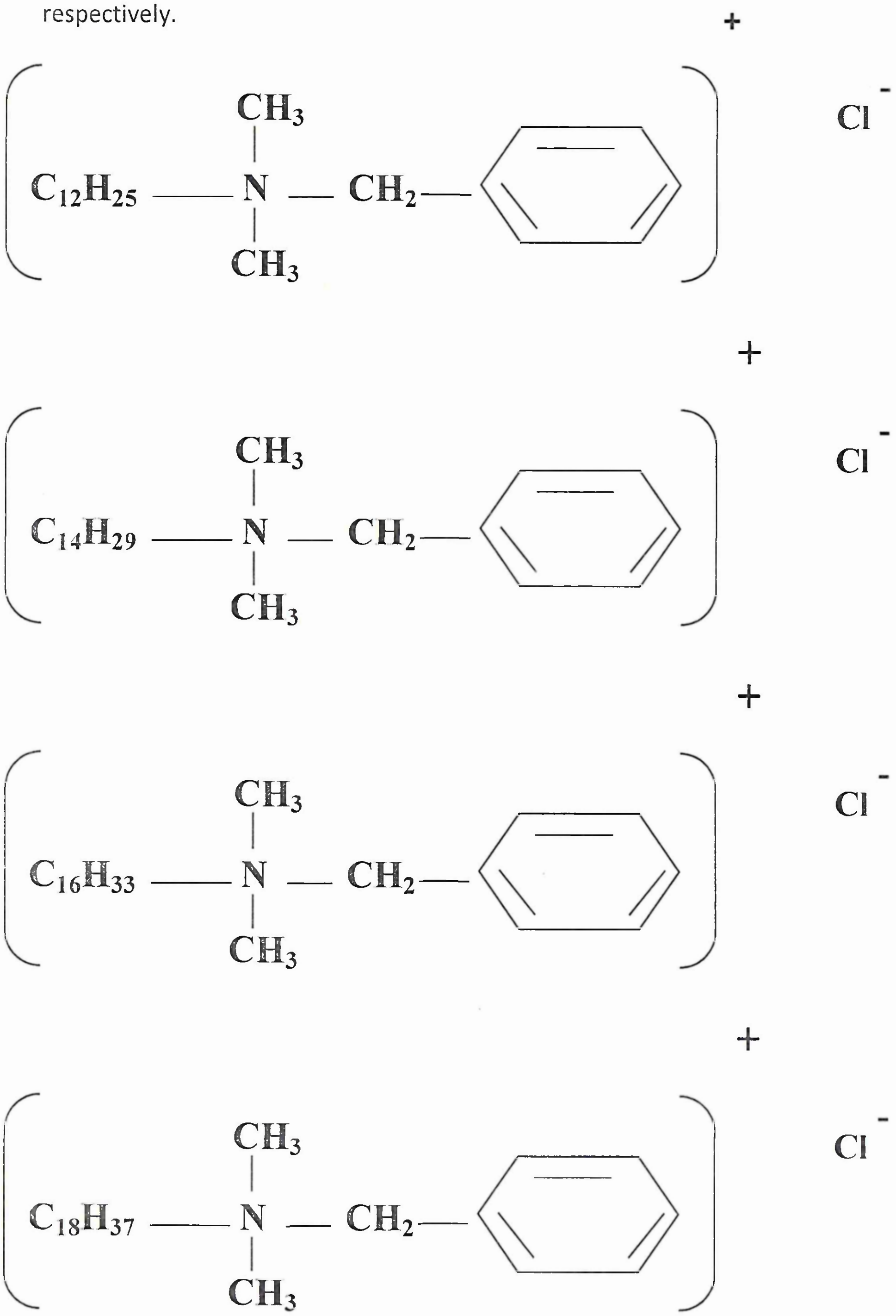


Figure 4.43 Chromatogram of carbon distribution of the oil extracted from the sample 4

Structure of quaternary ammonium compounds (Quats) C12, C14, C16 and C18 respectively.



Appendix B

- AL-Hamada oilfield pictures
- Photos of some of the experiments on the study samples (COD and PAH)

Figure 6.1 Lufkin pump of crude oil of AL-Hamada oilfield

Figure 6.2 S1 Sampling point of the well

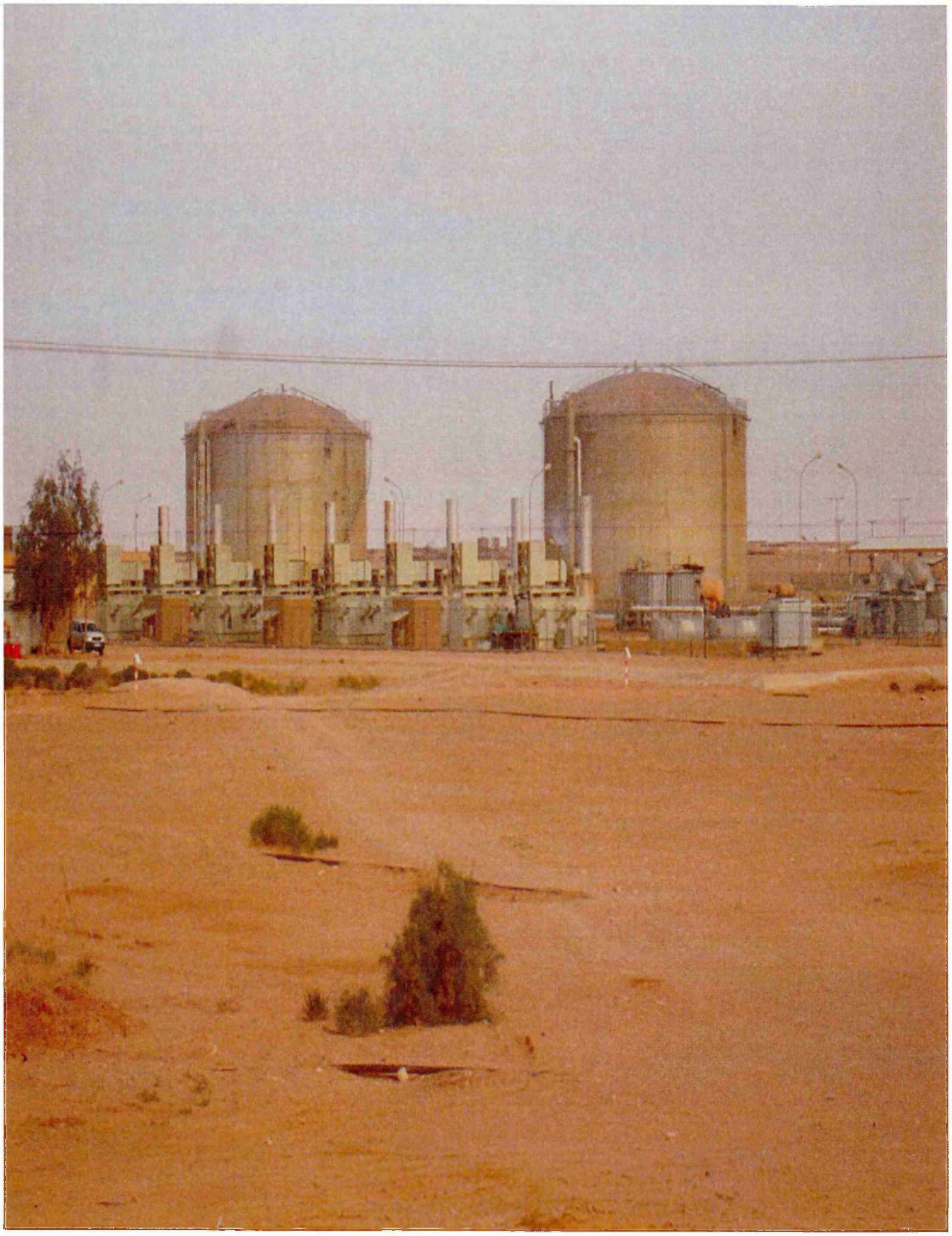


Figure 6.3 S2 The Oil Storage Tank

Figure 6.4 S3 AL Hamada oilfield Manifold Wells and The separation station.

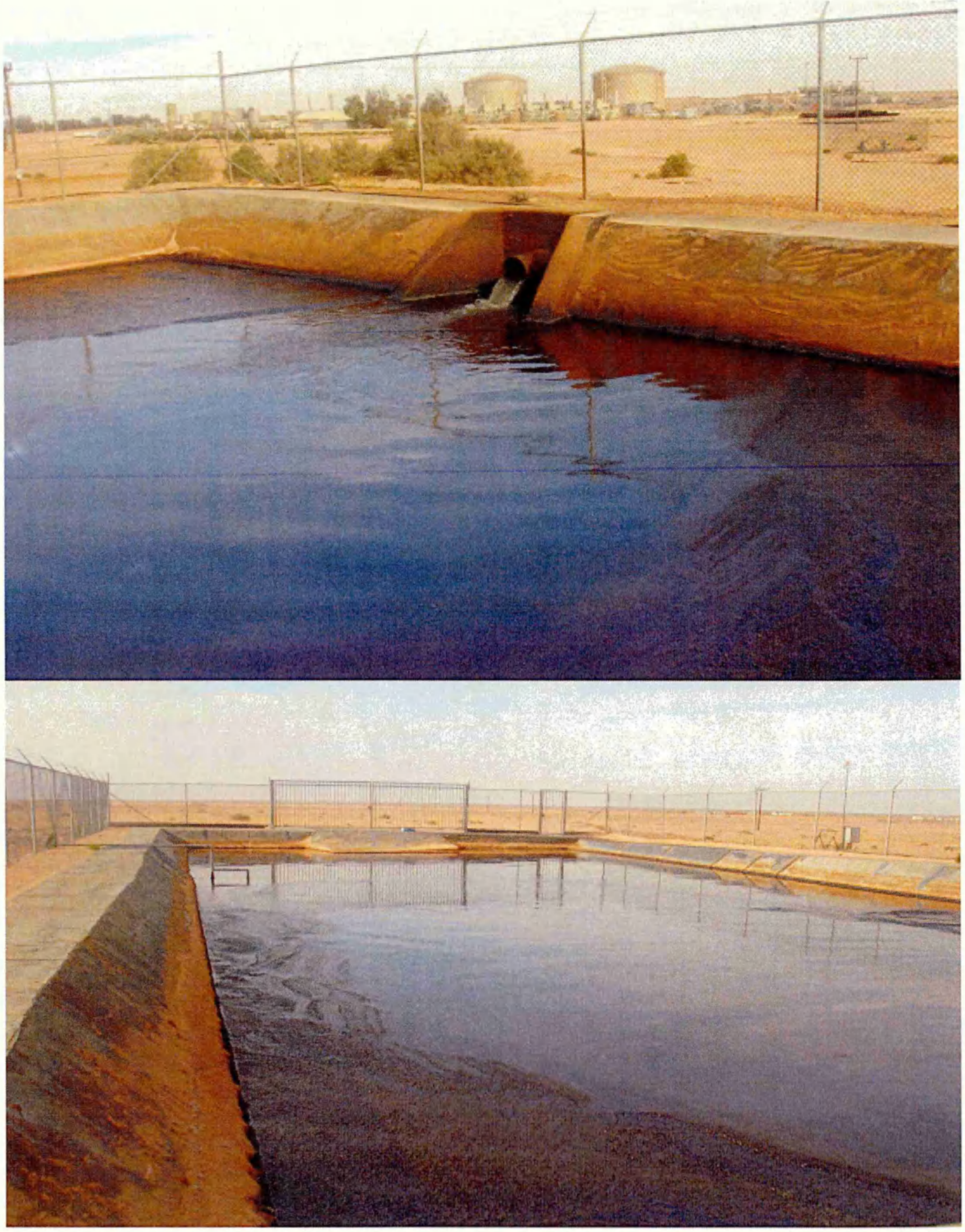


Figure 6.5 View of the 1st Pit of the Produced Water

Figure 6.6 S4 View of the 2^{nd} Pit of the Produced Water

Figure 6.7 Samples of the study Collecting points {S1 main stream, S2 main storage tank, S3 separator of crude oil, S4 the pit of produced water disposing (2nd Pit)

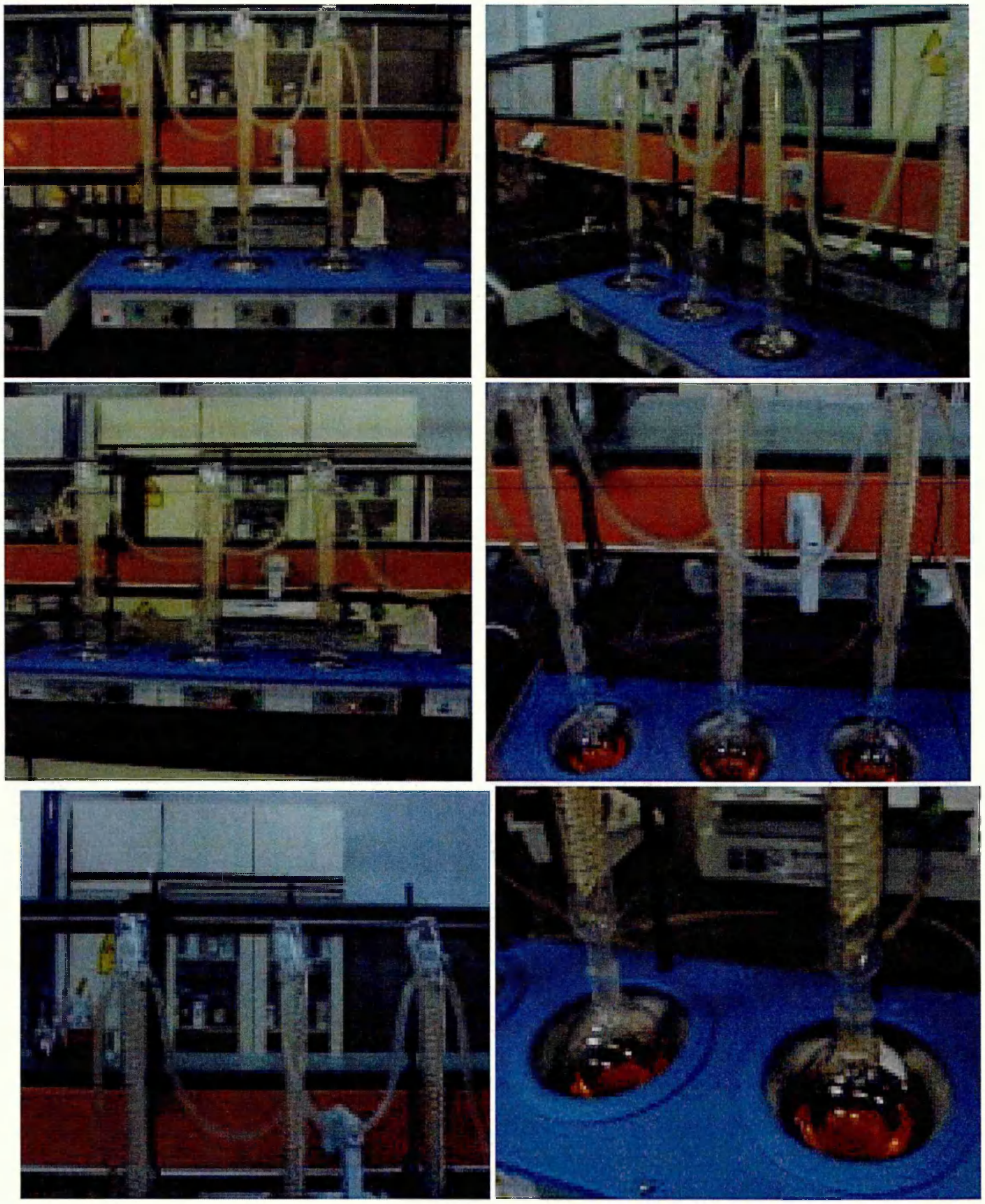


Figure 6.8 Samples analyzing work, COD determination steps (refluxed produced water samples and standard dichromate solution for a 2-h digestion period).

Figure 6.9 Sample analysing work, PAH determination steps (extracted and clean-up) .