TRIHALOMETHANE COMPOUNDS IN THE DRINKING WATER OF KUWAIT : A SURVEY FROM SOURCE TO CONSUMER

A Thesis submitted for the degree of Doctor of Philosophy

by

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THIS WORK IS DEDICATED TO MY
DAUGHTER JUMANA
AND
SON HUSSAIN

ABSTRACT

A comprehensive survey of the presence of trihalomethane (THM) compounds, as chlorination by-products, in drinking water in Kuwait have been performed. The survey covers the whole drinking water treatment cycle, starting with sea water and ending with the consumer tap. The data generated by the survey was all derived from actual water treatment plants, operating under normal conditions. All four trihalomethane compounds, namely; chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) were covered.

The study clearly showed that, although considerable amounts of THM compounds did form as a result of chlorination of sea water entering the multi-stage flash (MSF) distillation plants, these plants were highly efficient in removing these compounds. The average removal efficiency, based on THM compounds mass load in the sea water feed, was around 95%. Factors which were found to have an influence on the degree of formation of these compounds, include, chlorination practice (continuous vs. shock), sea water temperature, level of organic precursors and contact time. Of much more important consequence, as far as the presence of these compounds in drinking water is concerned, was the degree of THM compounds formation as a result of the chlorination of drinking water before it is pumped to the consumer. Here, not only all the compounds formed remain in the water but there is a definite tendency for continuous formation well after the actual chlorination process has taken place. Factors which were found affecting this formation include water temperature, contact time and chlorination dosage.

Although, all samples collected showed that the presence of THM compounds was always below the United States Environmental Protection Agency maximum contaminant level of 100 μg/L, *a need exists for the optimization of all chlorination processes with particular emphasis on the chlorination of drinking water. In almost all kinds of water encountered in this study, bromoform was found to be by far the most dominant compound.*

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PREFACE

The main objective of this work is to obtain reliable and relevant data concerning the fate of trihalomethane compounds formed during the chlorination of sea water used as feed in the distillation plants in Kuwait and the impact of the distillation process on such formation. For such data to be of any significance, it had to be based on real and actual operational conditions.

Having established an accurate insight into the behaviour of trihalomethane compounds within the distillation plants and the resulting concentrations of these compounds in the distillate product, the intention is to map the presence of these compounds through the subsequent treatment processes, which include blending and chlorination, ending with the consumer in representative locations.

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GLOSSARY

SYMBOLS

a - Constant

b - Constant

C - Concentration of *THM* Compounds (µg/L)

C_p - Specific Heat Capacity

D - Density (Kg/m^3)

DIS - Distilled Water

DOC - Dissolved Organic Compounds

DW - Distilled Water

H - Henry's Law Constant

L - Latent Heat of Evaporation (KW/Kg)

MD - Distillate Mass Flow Rate (Kg/h)

MF - Flashing Brine Mass Flow Rate (Kg/h)

MIGPD - Million Imperial Gallon Per Day

MSF - Multi-Stage Flash

MT - Mixing Tank

MV - Vent Gas Mass Flow Rate (Kg/h)

MW - Molecular Weight (g)

m - Mass Load of *THM* compounds (g/h)

p - Partial Pressure of a component (atm)

P - Total pressure in a stage (atm)

PS - Pumping Station

R - Ideal Gas Constant

RES - Reservoirs

S - Summer

SP - SPRING

T - Temperature (K)

THM - Trihalomethane

TOC - Total Organic Compounds

V - Vapour Release Rate in a Stage (m^3/h)

W - Winter
X - Mole Fraction of a compound in Liquid Phase
Y - Mole Fraction of a compound in Gaseous Phase

Subscripts

a - Above Demister in a Stage
b - Below Demister in a Stage
bd - Blowdown Brine Stream
c - Condensate
d - Distillate
de - Deareation Gases
f - Flashing Brine
g - Vent Gases From Stages
i - Individual *THM* compound
m - Make-up Feed
n - Stage Number
r - Recirculating Brine
v - Vapour
vg - Vent Gases
w - Water

CHAPTER ONE

STUDY BACKGROUND, SCOPE & OBJECTIVES

1.1 BACKGROUND

Due to the extreme shortage in natural water resources suitable for human consumption in *Kuwait*, a method had to be developed which is capable of producing the required quantity and quality of drinking water. This forced the country to turn to the sea as a source of drinking water supplies after proper treatment.

The concept was based on desalinating sea water by some appropriate means whereby the salt content is removed from it, leaving behind pure water which could be utilised after suitable further treatment as drinking water. The first time this concept was tried commercially in *Kuwait* and for that matter in the world was in the early *1950's*.

In the beginning, plants of small capacity of 2273 m^3/day (0.5 MIGPD) were installed. However, with the phenomenal increase of industrial activity in the country and the accompanied rise in the population partly due to vastly increasing work force, there was a continuous need to expand the capacity of the water desalination plants . By *1990* the total capacity of installed desalination plants in *Kuwait* was 7.142 Million m^3/day (262 MIGPD). In the last 40 years *Kuwait* has been recognised as a pioneer not only in applying sea water desalination technology but also in introducing numerous innovations and improvements related to both the design and operational aspects[1].

Different methods exist for the desalination of sea water. These fall mainly into two distinct categories; (a) thermal desalination or distillation processes which include multi-stage flash (*MSF*) distillation, multi-effect (*ME*) distillation and vapour compression (*VC*) and (b) membrane separation processes including reverse osmosis and electrodialysis. *Kuwait* sea water desalination plant technology has traditionally utilised the multi-stage flash (*MSF*) distillation process.

This process has proved to be the most suited to satisfy the requirements of the country, in addition to being the most reliable and cost-effective.

The product water produced by the distillation plants is by definition extremely pure and is, therefore, not suitable for human consumption. Drinking water in *Kuwait* is produced by blending the distilled water produced by the distillation plants with underground brackish water. The blending process is controlled in such a way so as to produce drinking water which is not only palatable but also conforms to **World Health Organisation** (*WHO*) guidelines for drinking water. Before the blending water is distributed to the consumer, the *pH* of the water is adjusted and adequate chlorination is applied as is the case in any public water supply.

The adverse effects of the presence of trihalomethane (*THM*) compounds in water supplies on public health has gathered momentum since the middle of the seventies when many studies discovered that the presence of these compounds above certain concentrations could lead to detrimental impact. *THM* compounds were considered as a direct result of the chlorination process which is the traditional method that has been used for many years to disinfect water supplies in order to ensure that consumed drinking water is free from any organisms which could be considered a threat to public health. The level of these chlorination by-products were, thus, dependent on the dosage of chlorine being applied, organic precursors in the water being chlorinated and finally factors such as chlorination process contact time, *pH* and temperature of the water.

Nearly all the above studies were carried out either in the *United States* or *Europe*. Maximum contaminant levels for total trihalomethane (*TTHM*) compounds were set which are continuously being reviewed and in the process of being made more and more stringent. Setting maximum contaminant levels for individual *THM* compounds are also contemplated. It is important to remember here that drinking water supplies in the above countries are mainly derived from lakes or rivers which are polluted and rich in organic content. This of course is a strong precursor for *THM* compounds formation during the water chlorination process.

Drinking water in *Kuwait*, as explained above, differs in two distinct ways from those of most countries. First, it is derived from the sea water and secondly the sea water from which it is derived undergoes a thorough distillation process. It is also characterised by the fact that starting with sea water and ending with drinking water two distinct chlorination processes are performed. The first is applied to the sea water before it enters the distillation plants and the second is applied to the blended water (distillate / brackish) before it is distributed to the consumers.

Very few studies have been carried out which deal with the specific circumstances which exist in countries which have the unique position of depending on sea water desalination for their public drinking water supplies. Most of the studies that tackled this subject were on the main laboratory studies which meant that they were very limited in content and thus suffer from serious shortcomings.

Only one study[2] examined the situation in *Kuwait*. This study was divided into two parts. The first part is an experimental laboratory programme aimed at the identification of some of the factors affecting the formation of halomethanes during the chlorination process of different types of water in *Kuwait*. The second part was a field assessment survey of the levels of halomethanes present in three different areas which contain distillation plants, within the different stages of the plant and in the drinking water supply network. The field assessment was limited to simply measuring halomethanes concentrations without establishing an appropriate mass loads balances which would enable the accurate determination of the fate of these compounds within the distillation plants. A simple correlation between these concentrations and relevant parameters such as residual chlorine, dissolved organic carbon and temperature was attempted based on what the experimental laboratory study revealed.

1.2 SCOPE

In order to accurately and systematically monitor the presence of *THM* compounds in drinking water in *Kuwait*, the scope of this study had to encompass the three distinct stages of its production. These are : sea water distillation, distillate / brackish waters blending and drinking water chlorination and distribution.

To generate relevant data with the required insight it was necessary to monitor the presence of *THM* compounds during the above three stages of water treatment simultaneously and for reasonably extended periods of time. It was very important to be aware of any operational factors during the treatment processes which might have an impact on the *THM* compounds formation and, thus, concentrations of these compounds and consequently to be able to determine such an impact. The ultimate aim was to generate enough data to enable the optimisation of the chlorination treatments so as to limit the concentrations of the generated by-products. This applies to both of the two distinct chlorination processes.

As far as the first chlorination process is concerned which is carried out on the incoming sea water entering the distillation plants, it is of particular importance to ascertain the way the distillation process determines the fate of any chlorination by-products. The influence of operational factors on the formation of *THM* compounds during the sea water chlorination process and during the actual distillation process must also be investigated. An insight into the way the nature of the distillation process with its characteristic conditions of low pressures, high temperatures, boiling, flashing, condensation and phase change, affects the fate of these compounds should be obtained. Finally, the concentrations of *THM* compounds in the distillate product and in the discharged sea water and blowdown brine must be determined as accurately as possible.

The second chlorination process occurs during or after the blending of distillate water with brackish water. The impact of this chlorination process coupled with the effect of adding brackish water and *pH* adjustment on further formation of *THM* compounds needs to be determined. Factors affecting this formation such as chlorine dosage, seasonal temperature variations and blending ratio must also be investigated.

The final stage of monitoring covers the actual distribution and supply of drinking water to the consumer. As it is very possible that further *THM* compounds formation could occur while the water is residing in the distribution network and storage reservoirs, it was important to measure the concentrations of these compounds at strategic locations within the drinking water distribution network and at specific consumer points. Again the impact of parameters such as chlorination level, contact time, seasonal temperature variations and rate of consumption is of fundamental importance.

1.3 OBJECTIVES

It is clear by now that the scope of this research work is quite extensive. The main objective is to be able to gain more insight and knowledge into the field of *THM* compounds formation in *Kuwait*. This means that the three distinct areas of water treatment, namely; sea water distillation, distillate / brackish water blending and drinking water distribution have to be investigated separately.

As it was the objective of this study to produce data and analysis which relates directly to the actual water treatments processes being carried out in the field, all samples that were used for analysis were taken from treatment plants under normal operating conditions and without any prior advance warning to the plants operating staff. It was also decided that for reasons of accuracy and reproducibility, all chemical analysis for *THM* compounds should be carried out by the author.

The research work had numerous objectives to achieve, with the intention of tackling them all with the aim of reaching a satisfactory conclusion concerning each one of them. These objectives are listed below :-

1. An important objective is to measure the concentrations of *THM* compounds in the distilled water produced by the multi-stage flash distillation plants under actual operational conditions. In addition the source of distillate contamination by these compounds and operational factors affecting their concentrations had also to be ascertained.

2. Another objective was to determine the impact of the level and regime of sea water chlorination process on the ultimate concentrations of *THM* compounds in the distilled water produced. On

the other hand the efficiency of the distillation process in removing *THM* compounds was also to be determined with the highest possible accuracy.

3. In order to map and thus understand the fate of *THM* compounds during the distillation process, a plant stage-by-stage analysis had to be attempted. This approach will not only provide what could turn out to be a very revealing insight into the whole subject concerning the fate of these compounds, but in addition will also enable the determination of the level of accuracy with regards to the whole analytical approach being utilised.

4. In addition to actually determining the concentrations of *THM* compounds within the distillation plant, it was very important to carry out a mass load balances of these compounds in each plant stream. This approach involves taking into consideration all the relevant plant streams volumetric flow rates and thus produces a much more significant picture as it allows the incorporation of important operational parameters. Furthermore, this approach allows quantifying the fate of *THM* compounds within the distillation plant.

5. Another objective which is made possible by adapting the mass load approach, is the determination of the amount of *THM* compounds being discharged to the sea and vented into the atmosphere. This objective is very important from an environmental impact point of view.

6. An important objective is to gain enough information to enable the optimization of the sea water chlorination process carried out at the intake systems of the distillation plants with the principal aim of reducing the amount of chlorination by-products production.

7. A further objective is to examine the impact of the blending of the distilled water produced by the distillation plants and brackish water from underground wells, taking into account the subsequent chlorination of the blended water.

8. A central objective is to monitor the formation and concentrations of *THM* compounds in drinking water being supplied to the consumer. The main aim here is to gain better understanding of the impact of all possible factors on the presence of these compounds.

9. The final objective is to be able to optimise the two chlorination processes in order to minimise the concentrations of *THM* compounds in drinking water supplied to the consumer.

CHAPTER TWO

LITERATURE SURVEY

2.1 Water Chlorination Practices

2.1.1 Historical Development

Chlorine gas was discovered in its gaseous state in *1774* by ***Karl W. Scheele***, a Swedish chemist[3]. Some years later *(1810)*, it was identified as a chemical element and was named from the Greek word *chlorous* (pale green), because of its characteristic colour. It was not, however, until several decades later that its use as a disinfectant was recognized.

Until the germ theory of disease was established (*around the mid-1880s*), odours were thought to be responsible for transmitting diseases, and so it was commonly believed that control of odours would limit the spread of infection. There is no question that the earliest applications of chlorine, beginning in about *1835*, were aimed at controlling foul odours, even though, because of the unsophisticated techniques used, the chlorinous odour imparted to the water being treated was sometimes just as, or more, objectionable than the odour it was meant to overcome. It was not until well into the *1890s* that chlorine and chlorine-containing products were evaluated and demonstrated to be effective disinfectants[4].

Water disinfection, as now ordinarily considered, involves specialized treatment for the destruction of harmful, and of otherwise objectionable, *"nuisance"* organisms. Classically, disinfection processes have been employed to destroy or inactivate disease-producing (*pathogenic*) organisms; more particularly, bacteria of intestinal origin. Such organisms can survive for weeks at temperatures near 21°C, or possibly even for months at lower temperatures. In addition to temperature influences, their survival in water depends on environmental, physiological and morphological factors, such as *pH*, oxygen and nutrient supply, dilution, competition with other organisms, resistance to toxic influences and ability to form spores. Water disinfection obviously also encompasses destruction of disease-producing organisms other than intestinal bacteria, but it does not necessarily imply complete destruction of all living organisms.

Within the last three decades, the functional advantage of treatment employing amounts of chlorine greater than those formerly considered adequate has become clearly appreciated. The wider adoption of continuous chlorine treatment can be expected to continue to develop in as much as high-rate chlorination provides means of achieving high standards of bacteriological quality and of improving operation of other water treatment processes. It is considered to be an integral part of any drinking water supply system, in addition to wide use in many other industries which utilises water in one way or another. The other important functions of chlorination, in addition to disinfection, include taste and odour removal; iron and manganese removal; hydrogen sulphide removal; colour removal; prevention of water quality degradation in distribution systems; control of biofouling in long transmission systems and cooling water systems; prevention and control of biofouling in filter media; restoration of wells capacity: and sterilization of water mains and reservoirs[5].

During the seventies, the significance of organic micro-pollutants in water supplies, became the source of much speculation. The main concern has been the possibility that low levels of organic chemicals in water supplies could cause long-term health effects, particularly cancer. The major source of these substances was considered to be pollution of raw water by waste water containing industrial and domestic effluents. A recent striking development has been the realisation that some of the more significant compounds to be found in water supplies, significant in terms of concentration and possibly health risks, arise in the treatment process itself and are more or less unrelated to pollution of raw water in the conventional sense[6].

2.1.2 Reaction Mechanism

Chlorine gas is dissolved in water directly or, by specially controlled process, in a solution containing caustic resulting in a hypochlorite bleach solution, to form hypochlorous acid (*HOCl*). The familiar hydrolysis reactions are represented as follows[7,8]:-

$$Cl_2(g) \rightleftharpoons Cl_2(aq) \qquad \text{Eq. 1}$$

$$Cl_2(aq) + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad \text{Eq. 2}$$

At ordinary water temperatures reaction given by *Eq. 2* is essentially complete within a time span of few seconds and even less at higher temperatures[9,10]. In dilute solutions and at *pH* levels above about 4, the equilibrium shown in *Eq. 2* is displaced to the right and very little chlorine exists in solution. In normal practice, the amount of chlorine supplied to water does not produce a concentrated solution of such strength as to yield such a low *pH*. The oxidising property of the chlorine is, however, retained in the *HOCl* formed, and it is also in this form that the principal disinfecting action of aqueous chlorine solutions occurs.

Hypochlorous acid ionizes or dissociates, a practically instantaneous reaction, into hydrogen and hypochlorite ions. The degree of dissociation depending on *pH* and temperature, according to the following reversible reaction :-

$HOCl \rightleftarrows H^+ + OCl^-$ Eq. 3

Hypochlorous acid is weak and dissociates poorly at levels of *pH* below about 6; thus, chlorine exists predominantly as *HOCl* at relatively low *pH* levels. Between *pH* 6.0 and 8.5 a very sharp change occurs from undissociated *HOCl* to almost complete dissociation. At 20°C and *pH* above about 7.5 or at 0°C and *pH* above about 7.8, hypochlorite ions (OCl^-) predominate, and they exist almost exclusively at levels of *pH* around 9.5 and above. The *pH* of chlorinated water supplies is normally within the range where chlorine may exist as both hypochlorous acid and hypochlorite ions. Chlorine existing in water as hypochlorous acid and hypochlorite ions is defined as free available chlorine.

Chlorine-containing compounds, such as calcium hypochlorite, $Ca(OCl)_2$, and sodium hypochlorite, *NaOCl*, ionize in water and also yield hypochlorite ions :-

$Ca(OCl)_2 + H_2O \rightleftarrows Ca^{++} + 2OCl^- + H_2O$ Eq. 4

$NaOCl + H_2O \rightleftarrows Na^+ + OCl^- + H_2O$ Eq. 5

The hypochlorite ions also establish equilibrium with hydrogen ions, depending on the *pH*, as shown by *Eq. 3*. Thus, the same equilibrium is established in water regardless of whether gaseous chlorine or hypochlorite chlorine compounds are employed. The important distinction is the resultant *pH* and hence the relative amounts of *HOCl* and OCl^- existing at equilibrium. Chlorine tends to decrease the initial *pH*, and hypochlorite tend to increase it.

It is evident from *Eq. 2*, that the hypochlorous and hydrochloric acids produced tend to lower *pH* and reduce alkalinity. Each part of chlorine added will neutralize not less than 0.7 part of alkalinity *(as $CaCO_3$)*, and may neutralize 1.4 parts, depending upon the extent to which *HOCl* is ionized and the manner in which chlorine is consumed by substances in the water. Hardness-producing materials, principally the carbonates and bicarbonates of calcium and magnesium, tend to buffer water against significant changes in *pH* that otherwise would accompany the addition of small amounts of acid or alkaline materials.

The reactions of chlorine with inorganic nitrogenous material, such as ammonia, are of great significance in water chlorination processes, especially disinfection. The kinetics of these reactions have been extensively studied. When chlorine is added to water containing natural or added ammonia, the ammonia reacts with *HOCl* to form various chloramines which, like *HOCl*, retain the oxidizing power of chlorine. The reactions between chlorine and ammonia may be represented[11,12] by the following :-

$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O$ Eq. 6
(Monochloramine)

$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O$ Eq. 7
(Dichloramine)

$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O$ Eq. 8
(Trichloramine or nitrogen trichloride)

The distribution of the reaction products is governed by the rates of formation of *monochloramine* and *dichloramine*, which are dependent upon *pH*, temperature, contact time, and initial *$Cl:NH_3$* ratio. In general, high *$Cl:NH_3$* ratios, low temperatures, and low *pH* levels favour *dichloramine* formation.

In sea water containing very low levels of ammonia, it is now well known that chlorine reacts with bromides to give hypobromous acid and hypobromite[13,14]. Bromamines may be formed from the hypobromous acid produced from bromide. The degree of halogen substitution on nitrogen will be determined by *pH* and the halogen:ammonia nitrogen ratio[15]. With 1 mg/L Cl_2 present, bromide ions naturally occurring in sea water reacts with chlorine, thus, producing bromine, which in turn reacts with ammonia according to the breakpoint reaction shown below :-

$$3Br_2 + 2NH_3 \rightleftarrows 6Br^- + 6H^+ + N_2 \qquad \text{Eq. 9}$$

Therefore, the consumption of oxidant correlates with ammonia level. With 1 mg/L Cl_2 and a $Cl:NH_3$ ratio less than 2, both combined chlorine and bromine are formed. The combined chlorine as well as the total oxidant concentration increases with ammonia concentration[16].

In unpolluted sea water, the ammonia concentration[17] is between 2.5 and 50 µg/L. High ammonia concentrations can occur, for example in harbour waters. ***Fiquet***[16] found at *Le Havre* power generation station ammonia concentrations of up to 1.5 mg/L. In these cases where ammonia nitrogen levels are sufficiently high, the formation of monochloramine[11,18] may compete with the bromide oxidation and a mixture of the haloamines may occur. This is especially important in cooling water chlorination because monochloramine is more persistent than combined bromine and, thus, may be the major component in the effluent[17,19-22].

Either the chlorine atom or the oxygen atom may act as the centre of electrophilicity for the reaction of $HOCl$ with inorganic compounds, for example, the oxidation of bromide ions, which probably occurs according to the reaction :-

$$HOCl + Br^- \rightleftarrows Cl^- + HOBr \qquad \text{Eq. 10}$$

The resulting *HOBr* is an electrophilic agent, but one that tends generally to react much more rapidly than *HOCl*. Much of the *HOBr* that reacts will be reduced to the bromide ions, to be reoxidised to *HOBr* by residual aqueous chlorine in the water[20]. The bromide ions concentration of most waters are quite low, so that the formation of *HOBr* is not significant. However, many river waters polluted with synthetic chemical wastes have been found to contain several tenths of a milligram per litre of bromide ions while sea water contains around 60 to 80 mg/L. Formation of *HOBr* is often the predominant aqueous chlorine reaction in sea water and saline estuarine waters[23]. Reaction with halogens would not involve iodide ions, since the abundant form of iodine in sea water is iodate ions in very low concentrations. Oxidation of fluoride ions would not be expected on thermodynamic grounds[21].

When *HOCl* reacts with organic compounds, either the oxygen or the chlorine atoms may serve as the centre of electrophilic action. Attack with oxygen results in formation of chloride ions plus an oxidised organic molecule. Attack by chlorine results initially in the formation of a chlorinated organic derivatives. Subsequent additional reaction or hydrolysis may give chloride ions in this latter case also. In any event the chlorine is reduced to a conventional *-1* oxidation state, for chlorine bound to carbon no longer has oxidizing properties[23]. What information there is indicates that 80-90% of the reduced chlorine reacts to give chloride ions and that 10-20% forms chlorinated organic compounds of some sort[24-26].

For dissolved organic nitrogen, it was reported[27] that in natural waters they comprised as much as one third of the total dissolved organic material and that their levels in natural waters can vary widely with water source and season, but that levels of 0.5 to 1.0 mg/L are not uncommon[28,29]. ***Gardner*** and ***Stephens***[30] found that 20% of the dissolved organic nitrogen in a marine water sample was in the form of amino-nitrogen compounds, whereas in a fresh water system, ***Tuschall*** and ***Brezonik***[27] found that as much as one-third was in the form of amino-nitrogen compounds.

Many studies[31,32] indicated that the presence of high concentrations of proteins and amino acids in natural waters seems to be related to algal activity. The nitrogenous organic compounds undergo special reactions with aqueous chlorine. The initial step is usually substitution at a nitrogen atom, typified by the following general reaction :-

$$R_1R_2CHNH_2 + HOCl \rightleftharpoons R_1R_2CHNHCl + H_2O \qquad \text{Eq. 11}$$

Such an initial step is often followed, however, by dehydrochlorination and hydrolysis to yield a carbonyl compound and ammonia, which proceeds through the breakpoint reaction or by additional chlorination, dehydrochlorination, and decarboxylation to give a nitrile or by rearrangement to give chlorine attached to carbon. Whatever the exact processes are, reaction with naturally occurring nitrogenous compounds appears to yield both substantial chloride ions and chlorinated organic carbon. Thus, the nitrogenous organic portion of the natural organic matter in water may constitute one of the significant sources of chlorinated organic compounds[33,34].

The type and concentrations of organic products from chlorination reactions are a function of the reactant concentrations, reaction kinetics and equilibria, *pH*, temperature, and presence of other halides like bromide ions or ammonia. Some products, *e.g. trihalomethane compounds*, appear to be a product of any reaction possible[35].

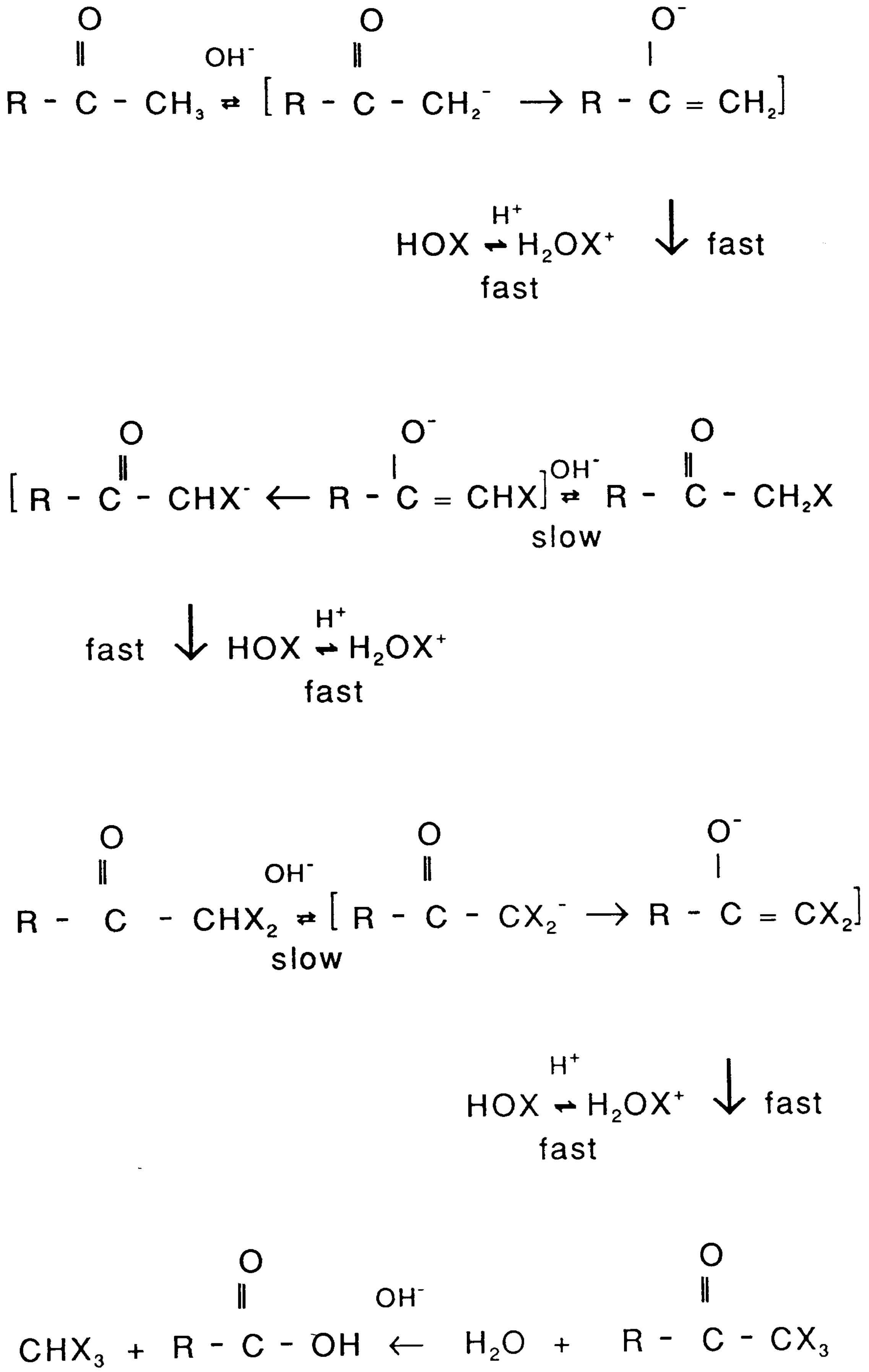
2.1.3 The Haloform Formation

Since the discovery of haloforms in water supplies and their production during chlorination processes by ***Rook***[36] and ***Bellar et al.***[37], many surveys have been carried out in an attempt to explain the reaction mechanism, the nature of the precursor substances in water that react with chlorine and the formation of brominated and iodinated derivatives and their occurrence.

The formation of trihalomethane *(THM)* compounds during chlorination of water is due to the reaction of aqueous hypohalites with methyl ketones or compounds oxidizable to methyl ketones to yield haloform. This is a classical reaction[22] of organic chemistry that has been known since *1822*. The pattern of the reaction is the successive replacement of hydrogen by chlorine on carbon alpha (α) to a carbonyl group followed by eventual hydrolysis to produce CHX_3 and generally, a carboxylate. The mechanism is believed to be an initial proton dissociation from the alpha carbon, giving an enolate carbon-ion, which is then subject to electrophilic attack by $HOCl$ or OCl^-. The diagrammatic representation of the course of the haloform reaction with hypochlorous acid and acetone is shown in **Figure 1**.

Essentially, the reaction shown in **Figure 1** consists of alternate hydrolysis and halogenation steps, with the first ionization step being rate determining[38]. It is likely that this is also the case for halogenation of natural aquatic humus[39].

A new thinking was initiated when ***Laidler***[40] stressed that kinetic relationships can be obtained only through measurements of changes in the initial rates of constants are varied. A start in this direction was made by ***Qualle*** and ***Johnson***[41] and by ***Gurol et al.***[42].



$$R-\overset{\overset{O}{\|}}{C}-CH_3 \overset{OH^-}{\rightleftharpoons} \left[R-\overset{\overset{O}{\|}}{C}-CH_2^- \longrightarrow R-\overset{\overset{O^-}{|}}{C}=CH_2\right]$$

$$HOX \underset{fast}{\overset{H^+}{\rightleftharpoons}} H_2OX^+ \quad \downarrow \text{fast}$$

$$\left[R-\overset{\overset{O}{\|}}{C}-CHX^- \longleftarrow R-\overset{\overset{O^-}{|}}{C}=CHX\right] \underset{slow}{\overset{OH^-}{\rightleftharpoons}} R-\overset{\overset{O}{\|}}{C}-CH_2X$$

$$\text{fast} \downarrow \quad HOX \underset{fast}{\overset{H^+}{\rightleftharpoons}} H_2OX^+$$

$$R-\overset{\overset{O}{\|}}{C}-CHX_2 \underset{slow}{\overset{OH^-}{\rightleftharpoons}} \left[R-\overset{\overset{O}{\|}}{C}-CX_2^- \longrightarrow R-\overset{\overset{O^-}{|}}{C}=CX_2\right]$$

$$HOX \underset{fast}{\overset{H^+}{\rightleftharpoons}} H_2OX^+ \quad \downarrow \text{fast}$$

$$CHX_3 + R-\overset{\overset{O}{\|}}{C}-OH \overset{OH^-}{\longleftarrow} H_2O + R-\overset{\overset{O}{\|}}{C}-CX_3$$

Figure 1 : **Haloform Reaction Pathway**[33]

Morris[43] stated that the classical haloform patterns may not be wholly valid for the reaction of aqueous chlorine with fulvate in water chlorination, and that the rate of ionization of acetone and of other simple methyl ketones, which have similar rates, is much too slow to account for observed rates of haloform formation with natural organic matter. Thus, some more active carbonion-forming centres, such as, acetylacetone and others, must either be present in the natural organic matter or must be formed through rapid preliminary chlorine oxidation reactions. The results of some studies, such as that of **Reckhow** and **Singer**[44,45], suggest that the total organic halides (*TOX*) is largely a by-product material, and that much of the *TOX* represents chlorinated compounds intermediate to eventual haloform production.

A number of factors could influence the haloform formation. These factors include the following :-

a) **Precursor Characteristics & Concentration**

Several classes of organic compounds in natural waters have been shown to be *THM* compounds precursors. Among these are fulvic and humic acids and their degradation products[36,46-51], agricultural drain[52], algal biomass[31,53-56], proteins, amino acids and purimidines[33,57], industrial effluents such as phenol[32,58].

Substantial evidence has been accumulated which indicates that humic substances constitute approximately 30 to 50% of the dissolved organic carbon in water[59], as it is the principal precursor of *THM* compounds and numerous other chlorinated organic species that are present in drinking water as a result of water chlorination[60-62]. Increasing the concentration of humic acid precursor in the presence of excess chlorine, with otherwise constant reaction conditions, causes *THM* compounds yields to increase in direct proportion to the humic acid dose[47,63].

b) Chlorine Dosage

The immediate chlorine demand is for the inorganic elements and compounds, like sulphide, iron[23] and ammonia because they react quickly with only traces of *THM* compounds being formed. Once the immediate chlorine demand is satisfied, the additional chlorine begins to react with any available organic matter. Within this region there is a nearly linear relationship between chlorine dose and the *THM* compounds level achieved. If enough chlorine is added to satisfy both the immediate and short-term organic chlorine demands, a long-term chlorine residual is obtained, and any further increase in *THM* compounds formation with chlorine dosage are rather modest. Presumably, the *THM* compounds formed at this stage are the result of incidental precursors formed during gross oxidation of the remaining organic material. Both similar[39,63-65] and contrary[66,67] results have been reported when conducting tests with different sources of precursors.

c) Contact Time

The formation of *THM* compounds under natural conditions is not instantaneous. Although, in some reactions the formation of *THM* compounds may be completed in less than an hour, in other circumstances, several days may be required before the maximum yield of *THM* compounds occurs[68]. Many researchers tried to measure the instantaneous *THM* compounds concentrations and the terminal *THM* compounds concentration in order to calculate the *THM* compounds formation potential, over certain contact times[69,70] or to determine the effect of contact time[63,71].

d) Temperature

Increasing the temperature has the predictable effect of increasing the rate of reaction[6,47,63]. ***Arguello et al.***[72] reported seasonal and temperature variations in *THM* compounds formation due to temperature changes. Instant *THM* compounds concentrations in finished water were lowest in winter and highest in summer. This observation was reported by many other investigators[47,69,73-77]. All agreed that this was due to faster reaction kinetics at higher *THM* compounds precursor concentrations in raw water in summer. This latter cause is due to enhanced leaching of organic material from decaying vegetative matter at warmer water temperatures.

e) **pH**

Numerous workers have shown that increasing the *pH* of the water being chlorinated may increase the formation of *THM* compounds during water treatment[47,49,67,77,78]. The increase in the formation rate with *pH* is expected, because the classic haloform reaction is base catalysed. Simple methyl ketones, which are models for the haloform reaction, have been shown to react too slowly to account for *THM* compounds formation under most drinking water conditions. ***Stevens et al.***[47], showed that at higher *pH* values, the simplest methyl ketone, acetone, reacts at a much higher rate, and this class of compounds could become a significant source of precursor in those *pH* ranges. An alternative explanation has been advanced which suggests that the macro-molecule may simply be *"opening up"* by mutual repulsion of the negative charges at high *pH*, thus, increasing the availability of additional reactive sites on the molecule[68].

f) **Bromide Ions Concentration**

Bromide ions are being recognized as an important precursor in the formation of *THM* compounds[39]. In the presence of chlorine, bromide ions are oxidised to intermediates[21], like, Br_2, *HOBr*, and

OBr^-, with some $BrCl$ and $BrCl_5$, which apparently participate in the halogenation step of the *THM* compounds reaction sequence much more effectively than does chlorine. This effect was observed by ***Kleopfer***[79]. The concentration of total *THM* compounds increases with the augmentation of bromide ions with the same amount of chlorine dosage. The increase in total *THM* compounds is up to two times higher than in the absence of bromide ions[80].

Trihalomethane compounds (*THM*) are formed during the chlorination of waters containing humic substances and other precursor compounds. Many researchers reported that chloroform is most often the predominant *THM* species, with brominated haloforms occurring[81] in waters containing bromide ions through the oxidation of bromide to hypobromous acid (*HOBr*) by hypochlorous acid (*HOCl*). Thus, when waters containing bromide ions are chlorinated, chlorinated and brominated *THM* compounds are formed. An important concern in *THM* compounds formation is the relative distribution of chloroform and brominated haloforms. It is well known that bromide ions concentration affects both the rate of formation and the species distribution of *THM* compounds[77,82].

Several researchers[77,82-85] have observed trends in species distributions as a function of initial bromide concentration when all other parameters are held constant. ***Cooper*** and ***Kaganowicz***[85] found that at Br^- concentration of 0.08 mg/L (10^{-6}M) in water, chloroform is the predominant *THM* compound formed at every *pH* except less than 5 while bromoform is below the detection limit or detected only at trace levels at *pH* 5 & 7, though it can be observed but at low concentration at *pH* 9 & 11. The concentration of total *THM* compounds increased with contact time and *pH*. By increasing the *Br*⁻ concentration in water to 0.80 mg/L (10^{-5}M), bromodichloromethane is the predominant species of *THM* compounds at *pH* 5 & 7, while at *pH* 9 dibromochloromethane predominates slightly over bromodichloromethane. At *pH* 11, initially the more brominated *THM* compounds, dibromochloromethane and bromoform predominated. With excess chlorine the chlorinated *THM* compounds, bromodichloromethane and chloroform, began to increase significantly after the *Br*⁻ ions are converted into organic bromine which takes 6 hours and 24 hours for bromoform and dibromochloromethane, respectively, for complete formation. At *Br*⁻ concentration of 8.00 mg/L (10^{-4}M) almost at every *pH* and reaction time, bromoform is the predominant *THM* compound. At *pH* 5, chloroform is formed at concentrations greater than the mixed halogen *THM* compounds. The concentration of bromoform and dibromochloromethane both increased with time and *pH*, as did the total *THM* compounds concentration measured as carbon. It has been reported that in general, when *Br*⁻ is present, the molar concentration of the *THM* compounds increases[32,86,87]. But ***Cooper*** and ***Kaganowicz***[85] reported that the addition of *Br*⁻ did not increase the total *THM-C* concentration.

2.2 Presence of Trihalomethane Compounds in Different Types of Water

2.2.1 Presence of Trihalomethane Compounds in Cooling Water

Power generation plants are probably the largest users of cooling waters. The type of water used differs throughout the world and could be either estuarine, marine, brackish or fresh water. Biofouling control through the use of disinfectants is an operating necessity for most power generation plants, in order to maintain acceptably efficient condenser heat exchange performance and to protect cooling water intake systems and structures. Chlorine is the principal biocide used for anti-foulant treatment of cooling water systems in electric power generation plants[88]. Studies have shown that chlorine and its residual by-products are toxic to aquatic organisms[89-91], and have considerable ecological impact on marine life due to the large volumes of cooling waters being discharged[92].

For these reasons, guidelines were proposed concerned with limiting the use and reducing the concentration of chlorine in power generation plants cooling water[93] and, in some cases, it was recommended that the exclusive use of chlorine should be discontinued where protection of aquatic life is of primary concern[94]. The main alternatives to chlorine gas disinfection could be grouped into the following categories[95] :-

a) chemical disinfectants with less adverse environmental impact compared to chlorine,
b) non-chemical fouling control techniques, and
c) detoxification of chemical anti-foulants.

Many researchers measured the chlorinated hydrocarbon level in cooling waters and observed that *THM* compounds are formed at the part-per-billion concentration level during the chlorination of cooling waters[96-99]. ***Jolley et al.***[98] conservatively estimated that the production of chloroform *(as a measure of total chlorinated hydrocarbons)* from chlorination of cooling waters by electric power generation plants in the United States was in the range of 100 to 200 tons per year in *1982*. ***Cumbie et al.***[100] on the other hand, calculated the total amount of chloroform released to the aquatic environment from the *USA* steam electric power generation industry to be approximately 32 tons for the same period.

Bean[96] reported formation of *THM* compounds at the parts-per-billion level in the chlorinated cooling waters of seven nuclear power generation plants throughout the United States. A complex mixture of halogenated phenols was also found in the discharges. The same conclusion was reached by ***Grove et al.***[101] after analyzing samples collected from the discharge of *Redondo* Power Generating Station located at King Harbour in the city of Redondo Beach, California. They concluded that no halogenated by-products other than haloforms and halogenated phenols, with bromoform the principal volatile component, were detected from the addition of chlorine to the cooling water.

Bean et al.[102] used a simulated biofouling control condition to differentiate halogenated organics ubiquitously present in natural waters in ten locations in the United States, and those produced during chlorination. They concluded that less than 1% of the added chlorine goes to the formation of haloform at all stations under study. This is lower than the 4% reported by ***Helz*** and ***Hsu***[103] during their studies of the halogenation of estuarine waters in closed containers. In addition, they[102] indicated that the amount of chlorine going toward production of lipophilic non-haloform halogenated material *(<800 molecular weight)* is substantially less than that going towards producing haloform. They also reported that attempts to identify individual halogenated components using capillary chromatography (*electron capture/mass spectroscopy*) have been generally unfruitful.

Rios[104] used laboratory apparatus to simulate actual cooling tower operating conditions as close as possible. He observed that *THM* compounds, methylene chloride, and 1,1,1-trichloroethane, were the only priority pollutants formed, and because of their volatility *THM* compounds will be stripped away by air in the cooling towers within several hours. Also, he reported that chloroform appears to be less volatile than bromodichloromethane and dibromochloromethane, and that chloroform continues to form in the discharged blowdown, which confirm the earlier results of ***Jolley et al.***[98]. The work of ***Helz et al.***[105] is the only comparison of laboratory simulation and direct sampling at an operating power generation plant that have been found in the literature. The authors concluded from their study that laboratory dosing of water taken from the intake canal with 1-2 mg/L chlorine as *NaOCl* provided poor models for what was observed in the field. On the other hand, ***Helz et al.***[92] found that 90% of the applied dosage (*1.5 mg/L chlorine*) to estuarine cooling water reacted very rapidly and was not discharged to the environment as chlorine.

Carpenter et al.[106] measured the residual chlorine in the water discharged at the *Port Everglades* power generation plant. Samples were collected from the pipe just downstream of the circulating water pump and from the discharge sluiceway, where mixing of chlorinated and unchlorinated water takes place. Chlorine is injected through a manifold in the intake structure and mixing takes place in the pump. They found that bromoform levels averaged 40 ppb and 65 ppb in the discharge water samples and in the intake water samples, respectively. The lower concentration in the discharged water was suspected to be due to dilution in the discharge sluiceway. It was also found that the products of chlorination were found to depend on the amount of chlorine added, with bromoform the major product, at doses of <1 ppm. With higher doses, the bromoform remained nearly constant *(300-400 ppb)* but several new peaks appeared in the chromatograms. This complies with what ***Carpenter*** and ***Smith***[107] reported that bromoform is the major product from the low level chlorination of salt water. And with what ***Luong et al.***[108] demonstrated that at low total organic carbon (*TOC*) concentrations (2.5 mg/L) and high bromide levels (2 mg/L), bromoform is the major *THM* species present. ***Helz et al.***[105] on the other hand, specified that brominated macro-molecular materials are produced in the discharged water.

Haag and ***Liwtzke***[109] developed a kinetic model to predict the concentrations of active halogen species in chlorinated saline cooling water. The model predicts that bromochloroamines could dominate in sea water, in contrast to the experimental results of ***Inman*** and ***Johnson***[18] which show the predominance of bromamines in chlorinated sea water. ***Figuet***[16] reported that during chlorination of sea water containing ammonia, the concentration and composition of residual oxidants depend on the chlorine-to-ammonia ($Cl:NH_3$) ratio, with combined chlorine and bromine residuals being formed at 1 mg/L Cl_2 and a chlorine-to-nitrogen (*Cl:N*) ratio of less than 2. However, ***Figuet's*** model did not account for chlorine demand for species other than ammonia.

Models have been developed that predict *THM* compounds formation as a function of water quality parameters, including temperature, *pH*, precursor source and concentration, chlorine dosage, bromide ions level, and reaction time[39,66,110-116]. These models are based on *THM* formed to chlorine consumed stoichiomertric relationships, as well as on empirical equations derived from linear and nonlinear regression analyses. The model of ***Engerholm*** and ***Amy***[113] predicts *THM* compounds formation as a function of *pH*, temperature, precursor concentration, and chlorine-to-*TOC* ratio. More recently, ***Amy et al.***[117] developed a multiple linear regression model as well as multiple nonlinear regression models to predict *THM* compounds formation. The latter model for reaction periods of 24-168 hours indicated the following order of importance:

Reaction time > Chlorine dose > *pH* > UV absorbance x *TOC* > Temperature > Bromide ions concentration.

Ali[2] and ***Ali*** & ***Riley***[118] carried out a field investigation of the levels of halomethanes in coastal sea water in *Kuwait* in areas likely to be affected by the release of chlorination by-products compounds discharged back to sea with rejected cooling sea water by different cogeneration power generation / water desalination stations. Since this was the first study of its kind to be carried out in *Kuwait*, all three areas in which the five then existing stations are located were covered in the survey. These included *Shuwaikh* and *Doha* areas in *Kuwait bay* in the central region, where *Shuwaikh, Doha East and Doha West* Stations are located and *Shuaiba* area in the southern region where *Shuaiba North and Shuaiba South* Stations are located.

The mean total trihalomethane compounds concentration in *Shuwaikh* area was found to be 10.8 ± 18.6 µg/L, ranging from a minimum of 0.1 µg/L to a maximum of 84.8 µg/L. The mean total trihalomethane compounds concentration for *Shuaiba* area was found to be 5.7 ± 5.7 µg/L, ranging from a minimum of 0.1 µg/L to a maximum of 25.2 µg/L. In the case of *Doha* area, the mean total concentration was reported to be 2.6 ± 4.1 µg/L, ranging from a minimum of 0.1 µg/L to a maximum of 20.4 µg/L. It is important to note that the above values refer only to bromoform ($CHBr_3$) and dibromochloromethane ($CHClBr_2$) compounds as other haloforms were not detected. In all locations, bromoform constituted about 95% of the total detected total trihalomethane compounds concentration. The dominance of bromoform was in agreement with previous studies performed elsewhere in the world[101,103,106-108], where bromide ions are present in high concentrations.

The above study found it difficult to attribute the variance observed in the concentrations of *THM* compounds among the three areas investigated to a single or a group of factors. However, it cited earlier investigations[35,98,119] which have identified several factors found contributing to the production and fate of volatile halogenated organics in rejected cooling sea water. These include the level of chlorine applied, the volume of cooling sea water rejected and rates at which they are released, the dilution capacity of the receiving waters, the presence of material that may compete for the halogens and factors related to evaporation and natural decay which is a function of UV light intensity. Of the above factors, dilution and reaction of the oxidants with material in the receiving waters seem to have the dominant effect[35].

The study did attempt to correlate the levels of *THM* compounds detected with other measured parameters. These include temperature, salinity, water sampling depth, current speed, wind speed, residual chlorine, ammonia, chlorophyll-α, suspended solids and dissolved organic carbon. The conclusion was that the correlation between the above factors and *THM* compounds concentrations was rather poor and did not reflect the results obtained under laboratory experimental conditions. This bad correlation coupled with the limited data available on the dynamics of water movement and other factors specifically related to each site made it difficult to attribute the observed differences to a single or a group of factors. However, after reviewing the study results it could be said that the concentrations of *THM* compounds detected were strongly related with the residual chlorine measured at each site.

In all three sites it was found that the highest concentrations of *THM* compounds occur near the immediate vicinity of the outfall structures of each station and that a subsequent dilution process occurs which is governed by the hydrography of each site including the effect of the wind-induced surface currents characteristics. Beyond the point of discharge, the distributions of these compounds were consistent with the hydrography of the area whereby concentrations falling to below the detection limit (0.1 µg/L) within a few kilometres. Another common feature was that higher concentrations of *THM* compounds were detected at the sampling points nearer to the outfall during the ebb phase as compared to the flood phase. This is possibly attributed to lower degree of dilution by the receiving water volume during the ebb phase.

2.2.2 Presence of Trihalomethane Compounds in Distilled Water

The presence of *THM* compounds in distilled water, produced by multi-stage flash distillation plants, is of some importance to most of the countries in the *Arabian Gulf* region, ,as it is the main source of drinking water. Distilled water is produced by thermal desalination of sea water. The produced distillate is then blended with certain amounts of brackish water to obtain palatability and to ensure compliance with World Health Organisation *(WHO)* standards on drinking water.

The presence of *THM* compounds in distillate was studied by ***Tawabini et al.***[63] on a laboratory bench scale in *Saudi Arabia*. They measured *THM* compounds in chlorinated synthetic sea water samples, distillate produced from chlorinated and unchlorinated synthetic sea water and from blended water of distillate with sea water before and after chlorination. On the one hand, they reported that *THM* compounds concentrations formed in the distillate of chlorinated sea water were in general lower than those formed in the distillate of unchlorinated synthetic sea water, while on the other hand, they reported that *THM* compounds formation in distillate produced from chlorinated synthetic sea water increased with increasing chlorine dosage. The conclusion reached was that the distillation process is a very effective means of removing *THM* compounds, total organic carbon *(TOC)* and chlorine. Formation of *THM* compounds was also observed upon addition of chlorine to the distillate.

Ali[2] and ***Ali*** and ***Riley***[120] studied the formation and distribution of brominated methanes in various stages of four different multi-stage flash distillation plants in *Kuwait*. They concluded that bromoform in the distillate product comprised 95-97% of the total brominated methanes compounds present, with lesser amounts of dibromochloromethane (2-4%) and traces of bromodichloromethane (<0.3%). In addition, he concluded based on semi-quantitative results of the analysis of samples taken from the vent gases, that over (98%) of the haloform formed was discharged to the atmosphere at the deareation stage, and that the total brominated compounds concentrations in the distillate varied from one plant to another and averaged 2.70-22.80 μg/L but rarely exceeded 30 μg/L.

A year long monitoring study was also carried out in *Saudi Arabia* by ***Mayankutty et al.***[121] to detect the possible presence of toxic organic compounds. The monitoring covered sea water feed, distillate product and potable water samples from *Al-Jubail*, *Al-Khobar* and *Al-Khafji* multi-stage flash distillation plants. The study did confirm that multi-stage flash distillation is a very efficient process in removing organic contaminants that may be present in sea water. The *THM* compounds concentrations detected in distillate and under-ground well water used for blending purposes were lower than the internationally agreed maximum limits by several orders of magnitude.

2.2.3 Presence of Trihalomethane Compounds in Drinking Water

The first report of the formation of chlorinated organics during treatment of drinking water came simultaneously from ***Rook***[36] in the *Netherlands* and from ***Bellar et al.***[37] in the *United States*. Both found that chlorine used for disinfection reacted with organic substances, so-called precursors, to form halogenated organics. The impetus for this relatively sudden development was the release of a study by the *United States Environmental Protection Agency (USEPA)* regarding the presence of potentially toxic organic substances in the *New Orleans* Water Supply[122]. In 1975 the ***USEPA***[60] undertook the *National Organics Reconnaissance Survey (NORS)*, which involved sampling the water supplies of some 80 cities, indicated that the occurrence of *THM* compounds in drinking water was widespread and results directly from the chlorination process. The concentrations of the four *THM* compounds surveyed (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) were found to range from high parts per billion *(ppb)* to sub-ppb with chloroform having the highest concentration and bromoform having the lowest concentration. Average levels of chloroform, bromodichloromethane, and dibromochloromethane were found to be 21, 6 and 1.2 µg/L, respectively. Since then ***USEPA*** has conducted a more exhaustive study, the National Organics Monitoring Survey *(NOMS)*[123] of more than 100 water supply systems. In each case, it was found that the occurrence of *THM* compounds in finished water was found to be widespread and is a direct result of chlorination. In general, the levels of *THM* compounds found in surface water sources greatly exceeded those found in chlorinated ground water sources, although some exceptions to this rule have been observed.

On November 29, *1979*, the ***USEPA*** promulgated a rule establishing a maximum contaminant level *(MCL)* for total trihalomethane *(TTHM)* compounds of 100 µg/L as a running annual average. In anticipation of this promulgation, ***Schreiber***[124] reported the results of a survey to determine the levels of *THM* compounds as well as trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, and carbon tetrachloride in the public water supply systems of *New York State*. Altogether, 235 grab samples were collected, the frequencies of detection and concentrations for the compounds were respectively, 89% and 62.7 µg/L for chloroform, 93% and 10.2 µg/L for bromodichloromethane, 57% and 3.0 µg/L for dibromochloromethane, and 0.47% and 0.3 µg/L for bromoform. The survey also indicated that carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene were detected in only two of the supply systems surveyed.

Then as early as January *1986*, ***USEPA*** indicated its intention to establish a new *TTHM* compounds standard[125] in the neighbourhood of 5-25 µg/L. As a result of the *1986* amendments to the *Safe Drinking Water Act (SDWA)*, data were gathered from 35 water treatment facilities regarding the levels of disinfection by-products *(DBP)*. *THM* compounds were the compounds with the highest concentrations and the median *TTHM* compounds value in this study[126] was 39 µg/L.

A number of surveys have been conducted concerned with the occurrence of *DBP* compounds in drinking water. A survey[127] carried out on tap water samples found seven *THM* compounds containing chlorine, bromine, and iodine. Also found in drinking water were compounds such as methylene chloride, dichlorobenzene, hexachlorobutadiene[128], tetrachloroethylene[129], trichloroethylene[128,129], carbon tetrachloride[122,128] and 1,2-dichloroethane[122,129].

Tardiff and ***Dunzer***[130] confirmed the presence of six halogenated compounds (viz, chloroform, bromodichloromethane, dibromochloromethane, bromoform, tetrachloromethane, and 1,2- dichloroethane) in drinking waters with concentrations ranging up to 100 µg/L. ***Glaze*** and ***Rawley***[70] conducted a study concerned with surveying the *THM* compounds concentration in drinking water of several *East Texas* under-ground water and surface water sources. They found that chloroform is the predominant of the *THM* compounds except in one under-ground system where brominated species were the predominant compounds.

Many researchers, in addition to being concerned with determining the level of *THM* compounds in drinking water samples, examined the seasonal variation in concentration and the precursors for *THM* compounds. Of those, ***Arguello et al.***[72] conducted a study to determine the concentrations of *THM* compounds in raw water, in water after initial introduction of chlorine, and in finished water from 14 utilities at monthly intervals for a period of one year. They observed that while *THM* compounds were present at widely varying concentrations in finished water supplies, these variations were not encountered to any appreciable extent in raw water. It was also found that *THM* compounds levels vary over a wide range in the finished water supplies of most utilities over the course of one year, with a trend towards lower concentrations during winter months. ***Singer et al.***[69] reported that *THM* compounds were formed during the course of chlorination treatment in nine large cities in *North Carolina*, and also that both seasonal and temperature dependence in *THM* compounds formation were observed. ***McGuire*** and ***Meadow***[131] reported the results of a national survey of *THM* compounds in drinking water and determined the extent and cost of compliance with the existing *THM* compounds regulations.

Many other surveys have been performed all over the world in order to monitor local situations. ***Aggazzotti*** and ***Predieri***[132] showed that volatile halogenated organics *(VHO)* are present in drinking water samples in *Italy* at low levels before any treatment, while after chlorination *VHO* appeared, almost exclusively as *THM* compounds, sometimes at fairly high levels (*maximum concentration* = 41.8 µg/L). For surface water samples, *VHO* appeared just as traces, seldom at high concentration (*maximum* = 263 µg/L).

Chambon et al.[133], undertook a survey in the *Rhone-Alps* region in *France* and showed that haloforms occurred in various water samples. Drinking water contained very low levels of haloforms, whereas surface water had significantly higher haloforms level; around 6 times more than drinking water. ***Norin*** and ***Renberg***[134] investigated 107 drinking water samples in *Sweden* and found that 95% of them contained 0.2-25 µg/L *THM* compounds. ***Sonneborn*** and ***Bohn***[135], performed a study on 27 different cities in the *Federal Republic of Germany*, which revealed that only chloroform was present above 1 µg/L, while the concentrations of the remaining haloforms fell within the nanogram per litre range.

Rebhun et al.[136], conducted a study of *THM* compounds levels in *Israel's* national water supply system, which is composed of open channels, open operational reservoirs, and a long closed conduit. The system is dependent on the high-bromide water *Lake Galilee* for its supplies. This was the reason given for bromoform being the most dominant *THM* compound detected. They observed that the major production of *THM* compounds occurred in the closed conduit rather than in the open channels due to the volatilisation of *THM* compounds.

Bertt and ***Calverly***[137] have conducted a 1-year survey in the *UK* of *THM* compounds concentration changes in a water distribution system. The survey was concerned with *THM* compounds levels at the point of consumption, not at the treatment plant. It was found that *THM* compounds increased significantly within the distribution system, where the treated water contained chlorine residual,*THM* compounds precursor, or both. The authors suggested that if *THM* compounds are to be measured for the purpose of ensuring compliance with proposed maximum contaminants levels, samples must be taken at the consumer's tap.

Trussel et al.[138] reported on a monitoring survey of *THM* compounds in the drinking water supplies of twelve countries. In all locations, *THM* compounds were detected with the exception of *Egypt*. The Egyptian samples showed the most industrial pollutants of any of the samples but not *THM* compounds despite the fact that a water treatment plant which utilises chlorine serves this location. The total organic carbon *(TOC)* content of the water was found to be 1.23 mg/L, indicating the probable presence of adequate naturally occurring precursor to form *THM* compounds. The conclusion is that the chlorination facility was probably not operating when the sample was collected.

Ali[2] and ***Ali*** & ***Riley***[139] reported that the mean concentration of brominated methane compounds found in *Kuwait* drinking water supplies was found to be 25.6 ± 9.1 µg/L with a maximum of 50 µg/L. The mean concentrations for the individual compounds were 13.6 ± 4.6 µg/L for bromoform, 8.8 ± 3.7 µg/L for dibromochloromethane,and 3.3 ± 1.5 µg/L for bromodichloromethane. They also indicated that water samples taken from roof-top storage tanks contained significantly less halomethanes than water samples taken from underground reservoirs.

2.3 Trihalomethanes Compounds Analytical Procedures

2.3.1 Sampling & Sample Preservation

It has become a cliche that :"*The results of any analysis are only as good as the sampling step*". Yet, this is a research area that has received the least amount of attention by analysts. The objective of the analysis should control the method of sampling[140].

The choice of grab versus composite sampling is a function of the objective of the sampling. This has been reviewed by ***Huibregtes*** and ***Moser***[141], along with the means to carry out both types of sampling procedures. In natural waters, samples show variability of concentration and type of compounds present. This has been shown in specific studies by ***Suffet et al.***, in the case of surface waters[142] and ground water[143]. Therefore, this variability must be taken into consideration when sampling. In surface waters, sample collection vessels for volatile organics consist of glass serum vials that are filled with water to overflowing and capped with *teflon-faced* septa that are held in place with *crimped-on* aluminum seals[144].

It has been shown that haloform formation continues in sample bottles, unless the sample is treated[144,145]. Water samples for haloform analysis can be preserved by adding ascorbic acid[146], potassium ferricyanide[144] or sodium thiosulphate to samples to destroy free-chlorine reactant. Chilling the sample with ice and analyzing within a few days after collection was also found to limit increases in haloform content[144].

2.3.2 Equipment & Reagents Selection

Equipment and containers for water sample collection, storage and processing should be constructed of glass or metal, if possible. *Borosilicate* glass is preferable because it can be baked at high temperatures to free it of any organic contaminants. *Stainless steel* is usually the metal of choice because of its inertness, resistance to corrosion and strength. Metals, such as *zinc* and *copper*, may cause catalytic changes of certain organic molecules, and aluminum reacts with alkaline water samples. *Teflon* can be used for flexible tubing and seals in bottles caps, but hydrophobic organic constituents may be lost from solution through sorption[146]. *Plastic* tubing, containers and filter membranes are the most common source of organic contaminants. Organic contaminants introduced into water flowing through polyethylene, polypropylene, black latex and polyvinyl chloride tubing have been determined by ***Junk et al.***[147] where organic contaminants concentrations ranged from 1 to 5000 µg/L.

Giam and ***Wong***[148] detected contaminants from glassware and *Teflon* equipment, stainless steel high-speed blender, filter paper, glasswool, aluminum foil and *Teflon-rubber* laminated disc *sample-bottle* seals in a gas chromatographic procedure for analysis of chlorinated hydrocarbons in sea water. Therefore, clean-up procedures are essential for any analysis.

Glassware and equipment should first be cleaned with a suitable detergent, followed by dilute hydrochloric acid[149] or chromic acid[150,151] and finally rinsed with distilled water. To remove completely any remaining organic contaminants, glassware should be heated in a muffle furnace to 400°C for 15-30 minutes[149] or 200°C[152]. Glassware and equipment not compatible with heating should be rinsed with redistilled acetone and finally with pesticide-quality hexane[149] or methanol[153]. **Moore** and **Karasek**[154] also reported that glassware can be cleaned by soaking in purified water and extraction with pure ether followed by a few millilitres of purified water.

Preparation of reagent water, free of organic contaminants is frequently one of the major challenges for recovery studies designed to test analytical procedures. ***ASTM***[155] *type II-grade* water is prepared by distillation, using a still designed to produce a distillate having a conductivity less than 0.1 µmohs/cm at 25°C. Multiple distillation in all-glass stills in the presence of potassium permanganate is frequently used to obtain reagent water of acceptable quality[148]. Distilled reagent water can be purified of traces of sorbable organic contaminants by passage through columns containing activated carbon[156-158], or activated carbon and other material like ion exchange[159] or *XAD-2* resins[153]. Double distilled water can also be purified by its extraction with *XAD-2* alone[152] or with *XAD-2* and *XAD-7* resins sequentially[154]. A spray-vaporisation technique was also developed by ***Chriswell***[160] to remove gas-chromatographable organic compounds from reagent water. Organic-free water can also be produced by controlled freezing of water[161].

In most cases, organic solvents suitable for trace organic analysis can be commercially obtained simply by specifying the grade of solvent. However, contaminants found in even the most highly purified organic solvents may interfere with certain analyses. If additional solvent purification is necessary in the laboratory, a wide variety of purification methods can employed like; distillation, by employing an effective column[153,162], or passing the solvent through a glass column filled with *activity 1-basic alumina*[163,164] or containing *Amberlite XAD-2* resin and granular carbon[165,166]. Some solvents like n-alkanes *(n-pentane through n-decane)* can be cleaned by passing through silver impregnated activated silica to remove unsaturated hydrocarbons and then be stored over phosphorous pentoxide[167].

Activated carbon, synthetic resins and semi-permeable membranes used to concentrate and separate organic materials from water, frequently contain preservation agents, wetting agents, unpolymerised material and other potential contaminants that must be removed before use. Activated carbon contains very little volatile material, because it is heated to a high temperature during its preparation. However, ***Van Rossum*** and ***Webb***[168], noting that activated carbon gave unacceptable blanks for certain analyses, found that pre-cleaning with chloroform reduced blanks to acceptable levels. They recommended on-column washing with acetone, chloroform and methanol. ***Grob***[169] suggested cleaning by immersion in carbon disulphide for 30 minutes, the process being repeated three times using new solvent, and then the same treatment is repeated with n-pentane.

Synthetic non-ionic resins, such as the *XAD* resins, frequently are supplied with salt preservatives in the resin beads, which must be removed by on-column washing with water before they can be used[170]. Many researchers recommended different cleaning methods for the *XAD*, which consists of *Soxhlet* extraction and by using the following solvents :-

- Methanol, acetonitrile and diethyl ether for 4 hours each[154], or 8 hours each[155,171-180] or 24 hours each[181];
- Methanol and diethyl ether, 6 hours each[152];
- Methanol, diethyl ether and acetone, 4 hours each[182];
- Acetone, diethyl ether and methanol, 4 hours each[183];
- Acetonitrile for 24 hours, then a fresh acetonitrile for 24 hours[184];
- Methanol, diethyl ether, acetonitrile and methanol, 16 hours each[185-188];
- Methanol, pyridine and diethyl ether, 8 hours each[189];

- Water, methanol, dichloromethane and again dichloromethane for 24 hours each[190-193].

An alternative method is on-column washing by placing the resin in a column and cleaning with different solvents[168,194,195]. On-column washing of *XAD* resins with 0.1N *NaOH* and 0.1N *HCl* was found to be necessary if *pH* adjustment is used during adsorption and desorption steps[196].

2.3.3 Isolation Techniques

A number of isolation techniques are now reviewed. More emphasis is given to the most important of them.

2.3.3.1 Freeze Concentration

Freeze concentration methods are applicable to polar, mono-functional acids, bases and neutrals of moderate-to-high volatility solutes. These compounds are frequently called volatile polar organics[197]. The technique is based on the theory that when the temperature is reduced, the aqueous and organic fractions freeze at different points. If the temperature is carefully controlled, the liquid organic fraction can be separated from the solid aqueous fraction by filtration. This technique simultaneously separates and concentrates the organic compounds without loss of volatile substances[198]. A number of different types of apparatus could be used for freeze concentration[199,200], but the most often used is the one designed by ***Shapiro***[199].

Freeze concentration is a very gentle preconcentration technique. It has not been extensively used for semi-volatiles because it does not isolate the solute from the matrix, it is relatively slow, concentration factors are limited by ionic strength of the sample and alternative pre-concentration techniques are frequently available[146].

2.3.3.2 Water Distillation

Distillation methods are applicable to the same volatile polar organic class of compounds discussed under freeze concentration techniques. A study conducted by ***Kuo et al.***[197] of the water distillation technique, used to concentrate volatile polar organics, determined that 80-90% of the mass of the compounds could be recovered in the first 10% of the distillate. By using a two-stage distillation process, concentration factors of 50 to 100 were possible. ***Chain et al.***[201] reduced the detection limit of volatile polar organics to the low part per billion level by combining distillation pre-concentration with gas-chromatographic analysis of head-space vapours above the distillate heated to 70°C. Even when high concentration factors are not obtained by distillation techniques, they may be useful because of their capability of isolating volatile polar organic solutes from inorganic and non-volatile organic constituents[202].

2.3.3.3 Membrane Techniques

Membrane techniques, such as osmosis, reverse osmosis and dialysis, have not experienced much use in analytical pre-concentration of organic constituents in water because low molecular weights *(<200)* and rapid diffusion rates of many semi-volatile solutes allow their passage through semi-permeable membranes. Specific sorption interactions of semi-volatile analytes with membranes also limit applicability of membrane techniques to certain classes of compounds.

However, membrane concentration techniques have the ability to process much larger volumes of water per unit time than solvent extraction, sorption techniques, evaporative techniques or freeze concentration[146].

2.3.3.4 Direct Aqueous Injection Technique

It is possible to inject a water sample directly into the gas chromatograph, without preliminary clean-up, and yet produce meaningful results[198]. The procedure allows the identification of compounds that are not amenable to other methods because they are too water-soluble[203]. Although, this method is less time consuming than methods involving a pre-concentration step, it is relatively insensitive and lacks selectivity between volatile and non-volatile components and is complicated by reactions that may occur at heated injection ports[204]. Low detection limits of about 100 µg/L have been claimed with an electron-capture detector and 5 µg/L with a gas chromatograph-mass spectrometer system[205,206]. ***Nicholson*** and ***Meresz***[207] measured *THM* compounds detection limit of less than 10 µg/L.

2.3.3.5 Head-space Analysis Technique

This method is not based on the analysis of the medium under study, but rather the analysis of a phase in thermodynamic equilibrium with it, generally the gaseous phase. This method is suitable for volatile organics and according to the method of their extraction, it can be divided into the three following groups[208] :-

a) **Static Head-space Analysis**

The sample for chromatographic analysis is taken from a closed vessel where the material under study comes into equilibrium with its vapour at a predetermined temperature. The static head-space analysis requires rigid control of the sample temperature, sample withdrawal and other parameters[209-211].

b) **Purge or Strip-Trap Technique**

The sample is taken from the gaseous effluent stripped through the material under study. Generally, this gaseous effluent is passed through a suitable trapping medium which is inert to the stripping gas. The volatiles are trapped and subsequently eluted, thermally or with solvent into a gas chromatograph.

c) **Dynamic Head-space Analysis**

The sample is taken from the gaseous effluent passed over the material under study. This dynamic head-space analysis is similar to the strip-trap procedure, but the equilibrium between the condensed and gaseous phase depends on the flow of the stripping gas and may not be well attained. The surface contact is smaller compared to the case of the strip-trap method. Either, it will take more time for the analysis, or the concentrate obtained may not contain sufficient amounts of the analytes to be detected. However, the technique is suitable for the head-space analysis of solids, which cannot be solubilised[212,213], or for samples that produce considerable foaming, especially biological fluids[214,215].

The first description of a purge-and-trap technique was given by ***Swinnerton*** and ***Linnenbom***[216], who stripped dissolved hydrocarbons from sea water by purging with helium and trapping the hydrocarbons in cold traps filled with activated alumina and activated carbon. ***Kaiser***[217] purged water samples with nitrogen, which was then passed through a gas-chromatographic column cooled with liquid nitrogen, resulting in volatile constituents being trapped at the head of the column.

Shortly after these early developments in purge-and-trap techniques, analysis of volatile organic components in head-space gas above a water sample was developed by ***McAuliffe***[218] and ***Rook***[128], who sampled static head gas after equilibrium with water at a certain temperature. ***McAuliffe*** analysed the gas phase directly, but ***Rook*** employed an activated-silica trap. ***Mieure*** and ***Dietrich***[219] continuously swept the head-space over the water with air, which was then passed into a porous polymer trap. ***Zlatkis et al.***[220] developed a similar technique that heated the water sample almost to boiling to volatilise the organic solutes into the head-space gas. They applied this technique to profile volatile metabolites in urine[221], while ***Dowty*** and ***Laseter***[222] used this method of head-space analysis to determine volatiles in drinking water. The carrier gas was sufficiently concentrated with volatile that no trap was required for additional concentration prior to chromatographic analysis. The simplest device yet designed for isolation of organic volatiles from water and introduction into the analyzer is a hollow fibre probe developed by ***Westover et al.***[223].

In spite of developments in direct head-space analysis of volatiles, ***Novak et al.***[224] claimed that sparging organic volatiles from water was several times more efficient than other extraction methods. They enhanced sparging efficiency by adding a salting-out agent to samples. More recent developments in volatiles analysis have centred on sparging coupled with various types of traps for concentration prior to analysis.

Grob[169] designed a closed-loop gas-sparging system that avoids high volumes of gas needed to remove compounds of low vapour pressure from water. A charcoal trap was used in the system. Advantages of this closed system are limitations on the amount of water vapour removed by sparging and a reduction in contaminants from the carrier gas. Organic compounds containing up to *24* carbon atoms were recovered by this system. Using this system coupled to a *capillary-column* gas chromatograph with *flame-ionisation* detector, certain organic compounds at the parts per trillion concentration level were analyzed in several waters[225]. The most recent refinements in equipment developed for closed-loop stripping procedure are given in a report by ***Grob*** and ***Zurcher***[226].

The purge and trap that has been most widely applied was developed by ***Bellar*** and ***Lichtenberg***[227] and has since been adapted for a commercial instrument[228]. The original procedure used only 5.0 mL of water, which was purged for 11 minutes with nitrogen without heating. The trap was filled with a porous polymer *(Tenax-GC)* that trapped organic compounds with a retention index greater than *500*. The trap after interfacing with an inlet of the gas chromatograph, was desorbed by heating to 130°C and back flushing with nitrogen. This method was limited to organic compounds that are less than 2% soluble in water and boil below 200°C. For the 5.0 mL sample, the useful concentration range was from 1 to 2500 µg/L for most gas chromatographs. The ***Bellar*** and ***Lichtenberg*** purge-and-trap technique was modified and scaled up for a survey of all possible identifiable volatile organic constituents in drinking water. Modifications are described in detail by ***Kopfler et al.***[144].

Various types of adsorbents for volatile traps have been investigated. ***Grob***[169] favoured a charcoal trap because of its low water affinity and thermal stability. The merits of graphitised carbon black as a trapping material were described by ***Raymond*** and ***Guiochon***[229]. The material proved to be stable at 400°C where compounds such as polynuclear aromatic hydrocarbons *(PAHs)* can be desorbed. Silica gel was found to be generally unsuitable because some aromatics containing above nine carbon atoms were irreversibly adsorbed and certain *olefins* were stereochemically rearranged[227]. Many styrene-divinylbenzene polymers outgas contaminants during thermal desorption. *Chromosorb 103* and *Tenax-GC* are acceptable porous polymers for volatile traps because of thermal stability[227]; these polymers have subsequently received the most use as trapping materials. The upper limit for desorption of paraffin hydrocarbons from *Tenax-GC* at 300°C was found by ***Ligon*** and ***Johnson*** for compounds containing *25* carbon atoms[230], who also designed a device for rapid thermal desorption of volatiles from the trap into gas chromatographs. A trap consisting of two-thirds *Tenax-GC* and one-third *silica* was used in the analysis of volatile priority pollutants in water[231]. However, ***Keith et al.***[232] found that silica gel degenerated after repeated usage and used *Chromosorb 102*, which gave acceptable performance in combination with *Tenax-GC*.

Cryogenic trapping techniques have also been employed to fractionate and recover organic volatiles in a gas stream. ***Vandergrift***[233] described using a thermal desorber, where the desorption is carried out using packed column flow rates, trapping the sample in a cryogenically cooled open-bore, 3m long x 4.2mm OD nickel trap. The main disadvantage of cryogenic traps is that organic volatiles with vapour pressures similar to those of water condense with water, whereas these same compounds are often isolated from water when sorbents are used as traps because of differences in affinity of water and volatile compounds for the sorbent.

The method of purge and trap was originally designed for use with packed columns. Their use with capillary columns is a fairly recent occurrence[234-237]. One of the problems that had to be overcome before capillary columns could be used was their very low flow rates relative to packed columns[238,239]. These low flow rates hinder the complete desorption and sample transfer to the capillary column.

2.3.3.6 Solvent Extraction Technique

Solvent extraction is the most commonly used method, where the extraction of the organic compounds from the water has normally been achieved by partition with a suitable immiscible organic solvent *(usually by shaking once or several times)*, which is then concentrated to an appropriate small volume for analysis[240,241]. Many old techniques of solvent extraction developed for processing large volumes of water[242] have been superceded by techniques that require water samples of small to moderate volumes and use small quantities of solvent[243,244].

A useful parameter for determining extraction efficiency of a solvent system for a particular solute is the extraction p-value *(fraction of solute partitioning into the non-polar phase of an equal-volume, two-phase solvent system)*. A simple device based on a *Mohr* pipette was devised by ***Bowman*** and ***Beroza***[245] to determine extraction p-values. In a series of three reports, ***Suffet*** used the p-value approach to determine the most efficient solvents and *pH* conditions for serial batch extractions of organophosphate pesticides for water[246], determination of optimum water/solvent ratios and number of extractions necessary for quantitative recoveries of certain pesticides and herbicides from water[247]. The third report contains the determination of optimal conditions for serial extraction of phenoxy acid herbicides from natural water[248].

Organic solutes whose p-value equals or exceeds 0.9 can be extracted from 1 litre of water with 95% recovery in five or fewer successive serial extracts of 50 or more millilitres of non-polar phase with a total volume of 500 mL of solvent[247]. However, there are some solvents which are recommended for liquid/liquid extraction techniques like pentane[249-251], iso-octane[252], methylcyclohexane[251], hexane[253], heptane or nonane. Another study[254] recommended a series of solvent systems in which the organic phase exhibits increasing polarity. These are :-

a) hexane or cyclohexane/ethanol + water
b) benzene/methanol + water
c) chloroform/methanol + water
d) ethyl acetate/water
e) butan-1-ol or butan-2-ol/water
f) phenol/water

Occasionally, the system used is of two immiscible organic solvents. All these solvents have low solubility in water. Except for pentane, all have a high boiling temperature, making it convenient to handle them at room temperature. It has been reported[255] that the extraction efficiency decreases in the order of pentane > hexane > hexane saturated with methanol > iso-octane > 15% *(v/v)* acetone in hexane > benzene.

Although batch extractions only require a separatory funnel for equipment, they are time consuming, can only handle a limited volume of water, and cannot be easily automated. ***Goldberg et al.***[256] designed a flow-through system whereby 8 L/h of water was extracted by a series of lighter-than-water and heavier-than-water continuous extractors of conventional design. An unlimited number of different extraction solvents could be used, an unlimited volume of water could be extracted and concentration factors of 105 were claimed. Continuous liquid/liquid extraction was coupled with continuous evaporative concentration in a system designed by ***Wu*** and ***Suffet***[257].

It featured a *teflon* helix mixing coil, a flow rate of 900 mL/minute, and a water-to-solvent ratio of 10:1. Greater than 80% efficiency compared to batch extraction was demonstrated.

Continuous solvent extraction can even be conducted in-situ at the sampling point at any desired depth. The apparatus, invented by ***Ahnoff*** and ***Josefsson***[258], consisted of two mixing chambers in series designed such that solvent extraction occurs in the upper part of the chamber, and phase separation occurs in the lower portion. Unfortunately, only very insoluble solvents can be used because slightly soluble solvents, such as diethyl ether, are lost to the water passing through the extractor.

Solvent extraction techniques for the analysis of volatiles in water have found limited application, because the volatile analyte is usually lost during the solvent concentration step that follows extraction. One approach is to extract with a low-boiling point solvent in a pressurized extraction apparatus. A second approach to solvent extraction of volatiles is to eliminate the solvent evaporation step by extracting with a small volume of solvent so that extracted volatiles are sufficiently concentrated for chromatographic analysis. In a relatively early method published by the ***Water Research Centre*** **(UK)**[259], 100 mL of water sample was extracted with 10 mL of petroleum ether *(redistilled from potassium hydroxide)* in a 250 mL separatory funnel by shaking for 5 minutes. Of this 10 mL extract, 5 µL were injected directly into the gas chromatograph. If required, the sample size can be reduced with a corresponding reduction in extractant volume. A blank determination of the solvent to be used was carried out for each batch of analysis.

Van Rensburg et al.[260] have described a rapid sensitive semi-automatic method for the determination of chlorinated organic compounds formed during chlorination of water, and of volatile halogen compounds appearing in surface and other waters. The method is based on a rapid liquid/liquid extraction process using hexane, and gas chromatograph analysis using an electron-capture detector. The linear detection range was from 0.3 to 300 µg/L with a lower limit of detection of 0.1 µg/L.

Mieure[261], ***Richard*** and ***Junk***[251], and ***Henderson et al.***[262] all developed methods of micro liquid/liquid extraction procedure involving the extraction of a small volume of water with an even smaller volume of organic solvent, followed by a gas chromatograph analysis of the extract with an electron-capture detector. ***Mieure***[261] used 1 mL of methylcyclohexane with a 5 mL water sample in a 9 mL screw-cap vial. The vial was sealed with an open top cap and a *PTFE* lined septum. ***Richard*** and ***Junk***[251] used 1 mL of iso-octane *(2,2,4-trimethylpentane)* with a 10 mL water sample in a 15 mL glass stoppered calibrated centrifuge tube. ***Henderson et al.***[262] on the other hand, used a 120 mL screw bottle filled to overflowing with water sample, so as to exclude all head-space. The bottle is capped with a *PTFE* lined septum and sealed by crimping with an aluminum retainer.

Dressman et al.[263] compared the Mieure method with the purge and trap method described by ***Symons***[264] and ***Bellar*** and ***Lichtenberg***[227]. They concluded that the results obtained by the liquid/liquid extraction and purge and trap methods are comparable to the extent that they are of the same order of magnitude on the same sample. Except for several samples having concentrations below 5 µg/L, the results generally do not vary by more than ± 15%.

2.3.3.7 Sorption Techniques

Techniques based on sorption of organic solutes from water can be used to concentrate solutes on the sorbents, desalt organic-solute fractions, partition the organic solutes into compound classes by selective sorption and desorption, and isolate solutes from water by desorbing with an organic solvent. Additional concentration can be performed by evaporating the organic solvent eluate. Sorption is a comprehensive term[146] including both adsorption *(solute bound at substrate surface)* and absorption *(solute solubilised within substrate).*

A wide variety of sorbents are available that can bind solutes by physical and chemical sorption mechanisms in various systems. In general, sorbents with most bonding mechanisms are the most efficient sorbents; however, they are often unsuited for analytical applications because sorbed solutes are difficult to desorb. For example, ***Suffet et al.***[142] found that granular activated carbon *(four sorption mechanisms)* was a much more efficient sorbent for removing volatile and semi-volatile trace organic solutes from drinking water than was the styrene-divinylbenzene *XAD-2* resin *(two sorption mechanisms)*. However, studies by ***Chriswell***[189] and ***Van Rossum*** and ***Webb***[168] indicated that *XAD-2* gave better recoveries for similar solutes at trace levels in analytical procedures requiring solute desorption compared to granular activated carbon because of irreversible sorption on carbon.

Activated carbon has a complex surface chemistry[265], which sorbs organic solutes very efficiently from water by multiple sorption mechanisms. Use of the carbon filter by analytical pre-concentration is decreasing because certain solutes sorbed on carbon have been shown to be oxidised and bacterially degraded during the carbon drying step of the carbon chloroform extract *(CCE)* procedure, certain sorbed solutes cannot be desorbed by chloroform or other solvents[168,189], more sensitive detectors have lessened the need for processing large volumes of water through a carbon filter, and better sorbents have been developed.

Amberlite resins[266] listed in **Table 1** are hard, insoluble, polymerized copolymer beads[267]. Each bead is formed from micro-beads cemented together during polymerisation, giving the resin a macro-reticular structure which results in a high surface area in each bed. *Amberlite XAD-1, XAD-2 and XAD-4* are styrene-divinylbenzene copolymers and function as non-polar, hydrophobic adsorbents, generally in the form of white beads. *Amberlite XAD-7* and *XAD-8* are an acrylic ester polymer, which is more polar and has a somewhat more hydrophilic structure than the *XAD-2* and *XAD-4* resins[154].

The adsorption of organic compounds on the homogeneous surfaces of these resins is a low energy binding process involving *Van der Waals* forces[154], so it is a physical rather than a chemical process[268], which allows for easy desorption of the adsorbed molecules. The *XAD* resins sorption-solvent elution method for concentrating and isolating semi-volatile solutes from water has been evaluated versus the carbon chloroform extract *(CCE)* method and solvent extraction method. *XAD* resins gave generally better recoveries than the carbon filter for most compounds tested[168,189], and of these resins an equal mixture of *XAD-4* and *XAD-8* was the most efficient sorbent[269]. *XAD* resins also compared favourably with solvent extraction procedures with the exception of aliphatic hydrocarbons, which were not efficiently sorbed on the resins[269].

XAD-2 was advocated by ***Burnham et al.***[270] as the sorbent of choice for concentration and isolation of a broad spectrum of neutral semi-volatile organic solutes from drinking water, river water, and ground

Table 1

Physical Properties of *XAD* Copolymers

SORBENT	COPOLYMER	AVERAGE SURFACE AREA (m^2/g)	AVERAGE PORE DIAMETER (Å)
XAD-1	STYRENE DIVINYLBENZENE	100	200
XAD-2	STYRENE DIVINYLBENZENE	330	90
XAD-4	STYRENE DIVINYLBENZENE	750	50
XAD-7	METHYL METHACRYLATE	450	80
XAD-8	METHYL METHACRYLATE	140	250

water. ***Burnham et al.***[271] demonstrated the utility of *XAD-2* and *XAD-7* for isolating trace semi-volatile solutes in drinking water, and ***Junk et al.***[153] developed a comprehensive procedure for isolating several classes of organic compounds at the part per billion level from water using *XAD-2* resin.

XAD-7 and *XAD-8* are characterised by higher column capacity factors due to more rapid adsorption kinetics of the moderately polar resins and by greater desorption efficiencies as a result of the absence of *α-bonding*, responsible for reduced recoveries of *XAD-1*, *2* and *4*. Steric factors are also considered important in this respect[272]. ***Dressler***[273] reported the different kinds of material that could be used as a sorbent. Tenax *{ poly (p-2, 6- diphenylphenylene oxide)}* was used by ***Leoni et al.***[274] to extract various pesticides and polychlorinated biphenyl *(PCBs)* from polluted natural waters at the 1ppm level. The main advantage of *Tenax* is its purity; no preliminary cleaning up procedure is necessary. A disadvantage is its high price.

Polyurethane foams have been very useful sorbents for *PCBs* and *PAHs* in water. Their first reported use was by ***Gesser et al.***[275] who concentrated *PCBs* on a foam plug in a sorption column and extracted the plug with hexane. ***Saxena et al.***[276] cited the advantage of high flow rate capabilities of foam adsorbents needed to process large volumes of drinking water that contained parts per trillion levels of *PAHs*. A limitation of polyurethane foam sorbents is that they efficiently sorb only semi-volatile solutes whose water solubility is extremely low[277].

Isolation of volatiles by sorption from aqueous solution has not met with much success, because the volatiles were invariably lost when the sorbent was dried to remove water, or when the solvent eluant from a sorbent column was concentrated by evaporation. The development of techniques for thermal desorption of volatile traps with the purge-and-trap techniques, led **Mieure** and **Dietrich**[219] to pack a column of *Chromosorb 102* for sorption of organic volatiles and semi-volatiles from water, then desorb this thermally to the inlet of a gas chromatograph. The main limitation of this procedure was the large amount of water that was introduced from the moist sorption column into the gas chromatograph. The water problem was circumvented by **Chang**[278], who first used *XAD-2* resin for sorption of water, then thermally desorbed volatiles and water from *XAD-2* to a *Tenax-GC* trap that retains only volatiles and allow water to pass. The *Tenax-GC* trap was thermally desorbed in the usual manner at the inlet of a gas chromatograph. Good recoveries at the low part per billion level for solutes as volatile as chloroform and as non-volatile as 2-methyl naphthalene were obtained. **Ryan** and **Fritz**[279] adopted the same procedure but using capillary columns. This resin extraction-thermal desorption procedure has great potential because it provides adequate sensitivity over a wide volatility range without the use of organic solvents. Also sampling and resin extraction can be accomplished simultaneously in the field.

Many solvents, both organic and aqueous, have been used to elute adsorbed compounds for *XAD* resins. Historically, the eluant used most often has been diethyl ether. The recoveries of several classes of compounds from *XAD* resins have been reported for several experimental conditions[152-154,189,203,271,280-285]. Diethyl ether has the advantage of being relatively non-polar while allowing for some polar interactions to occur via the oxygen and has been found to be quite effective in desorbing many classes of compounds from *XAD* resins. The disadvantages include flammability and reactivity to form side products such as 2-ethoxy-propane, hexane, hex-1-ene and 2-methylpentane[284]. ***Junk et al.***[153] stated that diethyl ether is about twice as effective as methanol in stripping all the sorbed components from the *XAD-2* resin, and it is also much better than carbon disulphide, pentane, hexane and benzene in the concentration process. On the other hand, ***Gustafson et al.***[286] postulated that of several organic solvents considered, methanol might be the solvent of choice because of its solubility.

n-Hexane has been used as an eluant to desorb compounds from *XAD-2* resin alone[287] or as a mixture with 15% acetone[192,288-293]. ***Tabor*** and ***Loper***[193] evaluated several solvent systems for elution efficiency using mutagenicity levels as a detection criterion and found that the 15% acetone in hexane system resulted in low blanks with corresponding high sample counts and so it was recommended for use over ether elution and acetone / dichloromethane sequential elution. Acetone was also used in combination with dimethylsulphoxide *(DMSO)*[185-188,294-296] or with dichloromethane *(DCM)* sequentially[193] or as a mixture. Carbon disulphide is a desirable eluting solvent because of its insensitivity to flame ionisation detector, which is helpful in detecting small amounts of solutes that appear near the solvent peak in the gas chromatogram[297]. ***Grob***[169] found that carbon disulphide is the best solvent to be used with charcoal (activated carbon). Other solvents have been used with activated carbon such as chloroform[298].

2.4 Utilisation of Organic Compounds in Multi-Stage Flash Distillation Plants

The formation of scale deposits on heat transfer surfaces is a problem encountered in many industries, and is one of the basic problems associated with the distillation of sea water. This is a highly optimised process and anything which upsets the heat balance is reflected sharply in the plant efficiency and, thus, product cost. Scale formation reduces heat transfer rates and increases pressure drop, necessitating periodic plant shutdown for descaling. Two types of scaling compounds can form in sea water evaporators; the alkaline scale which include calcium carbonate and magnesium hydroxide, and acidic scale which include three different forms of calcium sulphate.

2.4.1 Chemistry of Scaling Compounds

Scale deposits are formed by a process of crystallisation from a supersaturated solution. ***Partridge***[299], in a review of the literature prior to *1930*, stated that calcium carbonate and magnesium hydroxide precipitate as a result of carbon dioxide loss when boiler water is heated. This causes a shift from bicarbonate ion to carbonate and hydroxide ions. No further insight into the problem was gained until *1950* when ***Langelier et al.***[300] published their classical laboratory study on scaling in natural sea water. The alkaline scales are formed by reaction of the bicarbonate ions in sea water[301,302] :-

$$2(HCO_3)^- \rightleftarrows CO_3^{--} + CO_2 + H_2O \qquad \text{Eq. 12}$$

$$CO_3^{--} + H_2O \rightleftarrows OH^- + HCO_3^- \qquad \text{Eq. 13}$$

$$Ca^{++} + CO_3^{--} \rightleftarrows CaCO_3 \qquad \text{Eq. 14}$$

$$Mg^{++} + 2(OH)^- \rightleftarrows Mg(OH)_2 \qquad \text{Eq. 15}$$

At temperatures below 85°C, deposition of calcium carbonate following reactions according to *Eqs. 12 & 14* predominates. The form normally found in sea water is *aragonite*, rather than the stable *calcite*. This has been attributed to the adsorption of magnesium ions onto the scale nuclei[303], but there is also evidence[304] that an increasing concentration of sodium chloride favours aragonite formation. At temperatures above 85°C increasing proportions of magnesium hydroxide have been reported in scale deposits[305], due to the increased importance of reactions shown in *Eqs. 13 & 15.*

Calcium sulphate can exit in three crystalline forms; *gypsum* ($CaSO_4.2H_2O$), *hemihydrate* ($CaSO_4.1/2H_2O$) and *anhydrite* ($CaSO_4$). The stable form at temperatures above about 38°C is *anhydrite*, but crystallisation from sea water concentrates does not occur spontaneously, and the solubility limit of the metastable *hemihydrate* generally applies in sea water evaporators.

2.4.2 Scale Control Methods

The most commonly used method of scale control utilises the addition of a small amount of chemical compound to inhibit nucleation of scale and to disperse any solids in suspension so that they are readily removed with the blowdown stream. The chemicals which has been traditionally used are based on polyphosphates. Polyphosphates have the property of inhibiting the deposition of $CaCO_3$ from supersaturated solutions when added in 1-2 mg/L quantities and have been used since about *1936* for controlling scale in recirculating water systems. Polyphosphate based additives are, however, limited to temperatures below 90°C, whereby thermal degradation becomes excessive above this temperature. The degradation rate doubles for every 6°C rise in temperature, resulting in less polymerised material and ultimately producing orthophosphate[306]. The uncertainty in the optimum conditions for polyphosphate treatment results in extra cost due to increased down-time for cleaning, and also in capital investment cost in order to provide additional heat transfer area. Apart from the temperature limitations, polyphosphates are not effective in preventing calcium sulphate or magnesium hydroxide precipitation.

During the mid-seventies[307], a number of high temperature chemicals have been introduced as a result of research and development work to extend the range of additive dosing to higher brine temperatures. Chemicals based on polyacrylates were found to produce hard scale if certain temperature limitations were exceeded. Research work by *Ciba Geigy Company* and *United Kingdom Atomic Energy Agency (UKAEA)*[308] resulted in the development of *Belgard EV*, a low molecular weight polymalic carboxylic acid. Other manufacturers have since introduced chemicals of similar type. These polymers may act either as threshold inhibitors or by means of distorting the lattice structure of scale crystals, or both, so as to reduce adhesion to other crystals or to metal surfaces. Polymer dosing can be used either for new plant, or as an alternative treatment for existing polyphosphate or acid dosed distillation plants. It is often possible to increase distillate output from a polyphosphate plant by using polymer dosing at high temperatures.

The alternative to additive dosing is acid dosing, which was introduced in the *1960*'s as a means of raising top brine temperature above 90°C, so enabling plant output to be increased[309]. Acid is injected into the sea water feed make-up to neutralise the alkaline scale forming constituents, according to the following reactions[310] :-

$$H_2SO_4 + HCO_3^- \rightleftarrows CO_2 + SO_4^{--} + H_2O \qquad \text{Eq. 16}$$

Acid dosing is extremely effective, and can be used to the limit of calcium sulphate scale formation, so advantage can be taken of the cost reduction due to increased top temperature. However, careful control of acid addition is required to prevent corrosion[301].

2.4.3 Environmental Impact of Sea Water Distillation Plants

The interactions between the distillation plant and the environment lie in two major spheres. The first is concerned with the effect of polluted sea water and addition of certain chemicals during the distillation process on the distillate produced, while the second is related to the impact of the presence of the distillation plant on the surrounding environment.

The presence of pollution in sea water could lead to the contamination of distillate produced in addition to increased corrosion. Since the distillation process is a kind of evaporation under reduced pressure, there is some possibility for volatile pollutants to transfer into distilled water. Increased corrosion is due to the higher corrosive nature of these volatile pollutants.

The main impact of distillation plants on coastal marine life will be due to the large volumes of blowdown brine and cooling sea water discharged to the sea. Both will have higher temperature than that of sea water and the blowdown brine will have, in addition, higher salinity than sea water[311]. ***Krote***[312] tested *Belgard EV* anti-scalent for its ecotoxicology and reported that *"there is only negligible transfer of the product into distillate produced. Also, with an overall molecular weight of 500 to 5000 the product itself does not evaporate".*

Leimgruber[313] also tested *Belgard EV* and its neutralised form *Belgard EVN* for toxicity in distillation plants. The conclusion was that in a satisfactory operated plant, *Belgard EV* does not give rise to any toxic hazard in the distillate produced.

Due to the existence of large numbers of distillation plants on the shores of the Arabian Gulf and its closed nature, the accumulation of such chemicals may influence the whole natural life that is dependent on sea water. As an example, eutrophication can be caused by polyphosphates. Eutrophication is the promotion of excessive biological growth. Because of this problem some countries intend to ban phosphates for some applications[313].

Extensive ecotoxicological profile analysis which included evaluation of biodegradability, toxicity towards fishes, algae, and photomineralisation, has been carried out in the case of *Belgard EV*[312] which proved that the chemical had no adverse impact on the marine environment as a result of the expected amounts that might be discharged by distillation plants.

2.5 Health Aspects & Ecological Impact

Drinking water disinfection by chlorination was a decisive factor in combating infectious water-borne epidemic outbreaks. This is still true today, but the advantage of chlorination may be partially offset by the potential health hazards of non-infectious agents. Today, so-called mass diseases such as diabetes, rheumatism, cardiovascular diseases, hypertonia and cancer are prevailing. To discover the causes of these widespread diseases, factors such as the environment must be taken into account. Air, food and drinking water have to be observed. In most cases, only statistical means will reveal what relation drinking water has to these types of disease[314].

During the seventies, data was gathered which pointed to the possibility that the very chemicals being used to disinfect the water may be the responsible for causing certain diseases, with chlorine being a substance of primary suspicion. In the middle of the *1970*'s, the ***United States Environmental Protection Agency*** *(USEPA)* published results of a natural survey that indicated chloroform, a by-product resulting from chlorination, was a ubiquitous substance in water[315]. In *1976*, the ***National Cancer Institute*** *(NCI)* studies indicated that chloroform was an animal carcinogen[316]. Also other studies reached the same conclusion[317,318]. The National Toxicology Program study[319] indicated that bromodichloromethane is carcinogenic to rats and mice, dibromochloromethane is carcinogenic to mice but not to rats, and studies on bromoform are still in progress. Epidemiological data have since indicated an apparent association between chlorination of drinking water and the development of colon, rectal, and bladder cancers, with a possible risk ratio ranging from 1.13 to 1.93 being reported[320,321]. The most consistent finding was an association between bladder cancer mortality rates and *THM* compounds levels[322].

Many researchers reported that *THM* compounds are hepatoxins[100,316,323,324]. ***Hewitt et al.***[325] reported that bromodichloromethane and dibromochloromethane are weak hepatoxins compared to chloroform, while ***Agarwal*** and ***Mahendale***[326] found no evidence of hepatoxicity in rat for bromoform. ***Simon*** and ***Tardiff***[327] were unable to establish a mutagenicity for it, while bromodichloromethane and dibromochloromethane were found to be mutagenic, but they were not tested for carcinogenic activity.

McGuire[125] stated that the most recently published evaluation of the health effects of disinfection by-products by the National Research Council *(NRC)* supported the carcinogenicity of chloroform in rats. The *NRC*, however, discounted the original finding that chloroform causes liver tumours in mice, basing that conclusion on a more recent animal feeding study[328]. The *NRC* also concluded that chloroform concentration equivalent to a 10^{-6} *cancer-risk* should be increased from 0.2 to 5.6 μg/L. This more than twenty-fold change in the theoretical health risk of chloroform, illustrates the lack of conclusive scientific evidence in this critical area. In the case of the other disinfection by-products, including the three other *THM* compounds, insufficient valid data existed to warrant classification as carcinogens or to allow *cancer-risk* calculations.

A major point of interest here concerns the possible impact on the ecology of coastal waters and the resulting effect on the fisheries resources. The ecological impact involves either lethal effects due to direct contact with toxic agents or long-term changes which occur as a result of chronic exposure to pollutants. Despite the fact that a large number of studies have been conducted regarding the toxicological effects of chlorination by-products on the marine biota[90,329-335], relatively limited data is available about the toxicity of bromoform ($CHBr_3$) and dibromochloromethane ($CHBr_2Cl$). In some of these studies, factors such as *pH*, bromide ion concentration, forms and levels of nitrogen-containing compounds and dissolved organic carbon in the test water were not monitored or taken into account during the interpretation of the toxicological results[329,330].

Gibson *et al.*[331] have shown that at concentrations approaching 1 mg/L of $CHBr_3$, several near-shore marine species of clams, oysters, shrimp and fish survived. However, the bioaccumulation and depuration rates varied among individual membranes of a given species, between species and according to the levels of $CHBr_3$ in water. ***Trabalka et al.***[332] exposed crab embryos to various concentrations of *THM* compounds. Their data suggests that $CHCl_3$ was least toxic (LC_{50} of 116 mg/L), followed by $CHBrCl_2$ (119 mg/L), $CHBr_3$ (76 mg/L) and $CHBr_2Cl$ (53 mg/L).

Scott et al.[333] who exposed adult oysters to sea water containing an average of 25 µg/L of $CHBr_3$, reported that the exposed organisms developed reduced feeding responses, increased rates of respiration and reduced sizes of gonadal tissues. Rapid uptake of $CHBr_3$ into the tissues was observed with a bioaccumulation ratio of 5:1. However, complete depuration occurred within 96 hours. Although the feeding response returned to normal during the depuration period, the damage to gonadal tissues was found to be irreversible. This is in agreement with earlier findings of sensitivity of reproductive tissues and stages, especially sperms, to low levels of chlorination by-products[331].

Other possible effects of low levels of *THM* compounds in the marine environment include interference with the natural chemical communication system among some of the marine organisms. This is based on the increasing evidence that some halogenated organics, including $CHBr_3$ are being produced by certain marine species as defensive secretions or as sex hormones and thus the release of such compounds into the marine environment may affect the behaviour of these organisms[98,334-335].

CHAPTER THREE

ANALYTICAL PROCEDURE & PRACTICE

3.1 INTRODUCTION

After careful evaluation of the available techniques for the determination of the concentration of trihalomethane (*THM*) compounds, which were discussed earlier, *liquid/liquid* extraction was chosen as being the most suitable technique to be used in this research work. In particular, the technique of ***Henderson et al.***[262] was selected, pending further development and refinement, as the best candidate for optimising routine *THM* compounds analysis.

Due to the importance of following a standard testing procedure, *ASTM D3973-85* standard test method[252] was followed as much as possible. The test method described by this standard employs *liquid/liquid* extraction and can be used as a rapid and simple means of determining many volatile organohalides in raw and processed water. The applicable concentration range for *THM* compounds is from 1 to 200 μg/L. Detection limits depend on the compound under analysis, sample chemical matrix and on the characteristics of the gas chromatographic system.

3.2 Summary Of Analytical Method

The test method employs *liquid/liquid* extraction to isolate compounds of interest and provide around twenty three-fold concentration enhancement prior to measurement. A 139 mL aqueous sample is extracted once with 6 mL of solvent. A 1 μL aliquot of the extract is analysed in a gas chromatograph equipped with an electron-capture detector.

Extraction efficiencies with the 6:139 *solvent/sample* ratio for *THM* compounds averaged about 63%. To compensate for extraction losses, percentage recoveries were corrected by utilising fractional recovery of organic solvent at equilibrium and by extracting and analysing standards in an identical manner. The concentration of each *THM* compound is calculated and is reported in micrograms per litre (μg/L).

3.3 Experimental Set-up & Reagents

3.3.1 Experimental Set-up

The experimental set-up consisted of the following components :-

a) Extraction Vessel

A vial 145 mL in volume was used, equipped with *PTFE* septa and a twist cap with an opening which bares down on the septum to provide a positive seal instead of the aluminum crimp top. The vials were dyed black. This precaution was taken to prevent algal growth which would alter the organic composition of the sample upon standing and exposure to sunlight, which may cause further production of chlorinated organic compounds by photochemical reaction[249].

b) Sample Containers

1 litre amber glass bottles with *PTFE* screw caps were utilised.

c) Micro Syringes

5 and 10 μL in size.

d) Disposable Syringes

10 mL in size.

e) Glass-stoppered Volumetric Flasks
5, 10 & 100 mL in size.

f) Perkin-Elmer *Sigma 15* Gas Chromatograph
equipped with ^{63}Ni electron-capture detector.

g) Gas Chromatograph Columns
A 3.175 mm inside diameter by 3.048 m long stainless steel column packed with *10% SE-30* on *80/100 mesh Chromosorb W-AW* and operated at an initial oven temperature of 55°C which was eventually increased to 95°C at a rate of 2°C/min. The injection port and the detector were maintained at temperatures of 250°C and 350°C, respectively. The carrier gas *(argon with 5% methane)* was supplied at a flow rate of 30 mL/min as make-up to the electron capture detector. The instrumentation configuration include moisture, carbon and oxygen traps on the carrier gas line.

3.3.2 Reagents

A number of reagents were employed, which included the following :-

a) Extraction Solvents
It is important to ensure that reagents are of sufficiently high purity to permit their use without lessening the accuracy of the determination. Many reagents were tried, but it was found that Hexane *(99.9% Fluka for HPLC)* contained the least impurities.

Impurities in the extracting solvent can be a source of interference. Volatile compounds, that are extractable and responsive to electron-capture detection, may interfere with the analytical method. For this reason, solvent blanks were analysed daily and before a new bottle of solvent is used for the first time. Whenever interfering compounds were traced to the solvent, impurities were removed by double distillation[153,162].

b) Pure Water

Organic free water was prepared by boiling the double distilled water for 15 minutes, while allowing pure nitrogen to bubble through it, in order to purge any contamination that might still be present. The water produced was collected in amber clean bottles and kept in the refrigerator for no more than two days and checked before each usage[238].

c) Detergents

Suitable detergents for laboratory glassware were utilised.

d) Reference Standards

Reference standards of chloroform, bromodichloromethane, dibromochloromethane and bromoform were used.

e) Stock Solutions

Stock solutions of between 2 to 10 mg/mL for each standard were prepared as follows :-

- a 100 mL ground-glass-stoppered volumetric flask was filled with approximately 80 mL of hexane.
- the flask was allowed to stand unstoppered for about 10 minutes or until all the hexane wetted surfaces are dry.
- the unstoppered flask was weighed to the nearest 0.1 mg.
- two drops of one of the standards were immediately added to the flask using a 10 µL syringe, before the flask was reweighed. Care had to be taken to ensure that the drops fall directly into the hexane without contacting the neck of the flask. The other

three standards were added in the same way.

- the volume was now diluted with hexane, stoppered, then mixed by inverting the flask several times.
- the concentration in micrograms per millilitre was then calculated from the net gain in weight of each compound.
- the prepared solutions were then stored at 4°C. Before use they were warmed to room temperature.

3.4 Sampling Procedures

Sampling procedures were considered to be very important as they affect the accuracy of analysis. Therefore, certain measures had to be ensured, which included the following :-

3.4.1 Sampling Bottles & Extraction Vials Preparation

Sampling bottles and extraction vials were prepared by washing them with detergent water, rinsed with tap water, then washed with chromic acid and finally rinsed with organic free water[150,151].

The sampling bottles and extraction vials were allowed to air dry, then left in an oven at 120°C overnight and were then allowed to cool in an area known to be free of organics. When bottles were cold, they were sealed using supplied caps.

3.4.2 Sample Preservation

Although in some samples residual chlorine was detected, no chemical dechlorinating agent was added. However, all samples were chilled to below 4°C by keeping them in an ice chest during transportation from the sampling location to the laboratory[144]. Furthermore, analysis for *THM* compounds was carried out as soon as possible after sampling time. In all cases, this was done within one hour of sampling time.

3.4.3 Samples Collection

Samples were collected in sampling bottles requiring transfer to extraction vials as part of the analysis. This procedure was adopted to permit replicate analyses. The procedure which has been validated by interlaboratory testing is described below.

The sampling bottles were filled in such a manner that ensures no air bubbles pass through the sample during filling. The bottles were filled to overflowing and was then placed on a level surface. The *PTFE* side of the septum was positioned on the convex meniscus and bottles were sealed by screwing the cap on tightly. The bottles were then inverted and the caps were lightly tapped on a solid surface. The absence of entrained air would indicate a successful seal. If bubbles were present, the bottles were opened and few additional drops of water added. Sampling bottles were then resealed and this seal was maintained until analysis time.

All samples were collected from water taps. In all cases the water flow rate was fixed to allow the system to flush. When the temperature of the water had stabilised, the flow was adjusted to about 500 mL/min and samples were then collected from the flowing stream.

3.5 Calibration & Standardisation

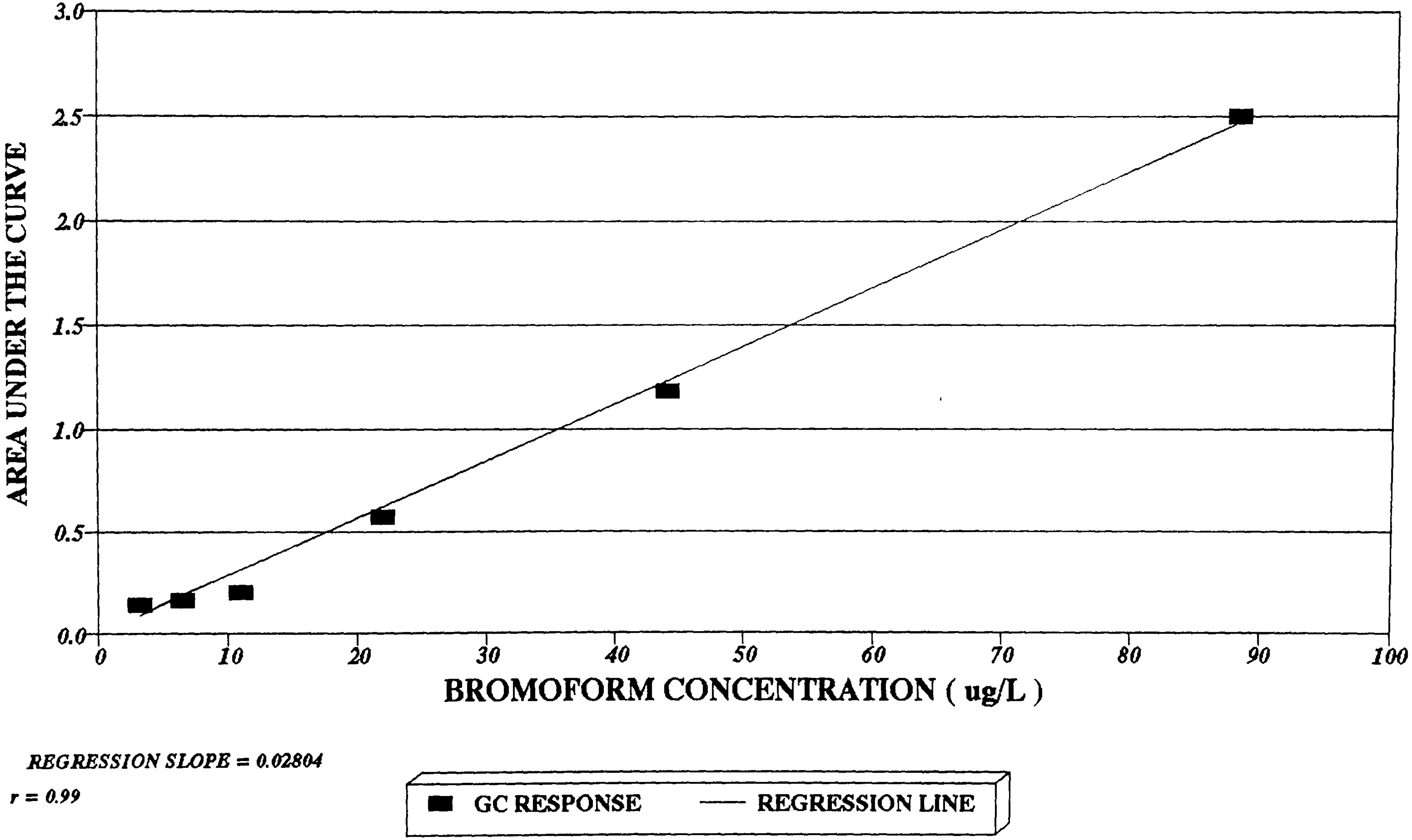
Calibration and standardisation was ensured by preparing, from stock solution containing approximately *10000* times the expected water concentration, a series of dilutions until no peaks were recorded by the gas chromatogram. A 1 μL of each of the above dilutions were injected into the *GC-ECD*. The generated data were used to construct a regression curve enabling the determination of the concentration of a component from the displayed *GC* peak. A sample of such regression curve is shown in **Figure 2**. Regression curves were continuously up-dated every two weeks or whenever found necessary.

Meanwhile, a standard solution of the four *THM* compounds in hexane were prepared daily at concentrations similar to what is expected to be found in the analysed samples. The response of the *GC-ECD* was compared to the standard solutions, thus, verifying the regression curve validity.

3.6 Analytical Procedures

After filling the extraction vials with water sample until overflowing so as to exclude any headspace, the vial was then capped with a *PTFE* lined septum and sealed with a screw cap. To the water sample in the vial, 6 mL of hexane solvent was added by piercing the septum with needles of two disposable syringes. The first syringe containing the solvent while the second was empty. As the hexane was added to the sample, the displaced water was collected in the empty syringe. The vial was then shaken vigorously for 25 minutes, using a platform shaker with 950 cycles per minute. Finally, the vial was allowed to stand for at least 1 minute to allow phases separation.

FIGURE 2
STANDARD REGRESSION CURVE



REGRESSION SLOPE = 0.02804

r = 0.99

A sample volume of 1 µL of the upper (*organic*) phase was then injected into the gas chromatograph, using a 5 µL *Hamilton* syringe. Care was taken to ensure that no droplets were drawn into the syringe. The analytical procedures end with the recording of the area of each peak of interest. A sample chromatogram of the results obtained is shown in **Figure 3**.

3.7 Data Calculation & Analysis

The concentration in micrograms per litre (µg/L) for each component in the sample was obtained using the method suggested by ***Hertz*** and ***Suffet***[140]. *Liquid/liquid* extraction methods are based on the distribution of solutes between two immiscible liquids. The fraction of solute that partitions into the organic phase is defined as follows :-

$$\boxed{E = \frac{(A_n)(V_n)}{(A_s)(V_s)}} \quad .... \quad \textbf{EQUATION 17}$$

where

E - the fraction of solute that partitions into the organic phase.

A_n - amount of analyte in organic phase.

A_s - amount of analyte in water phase.

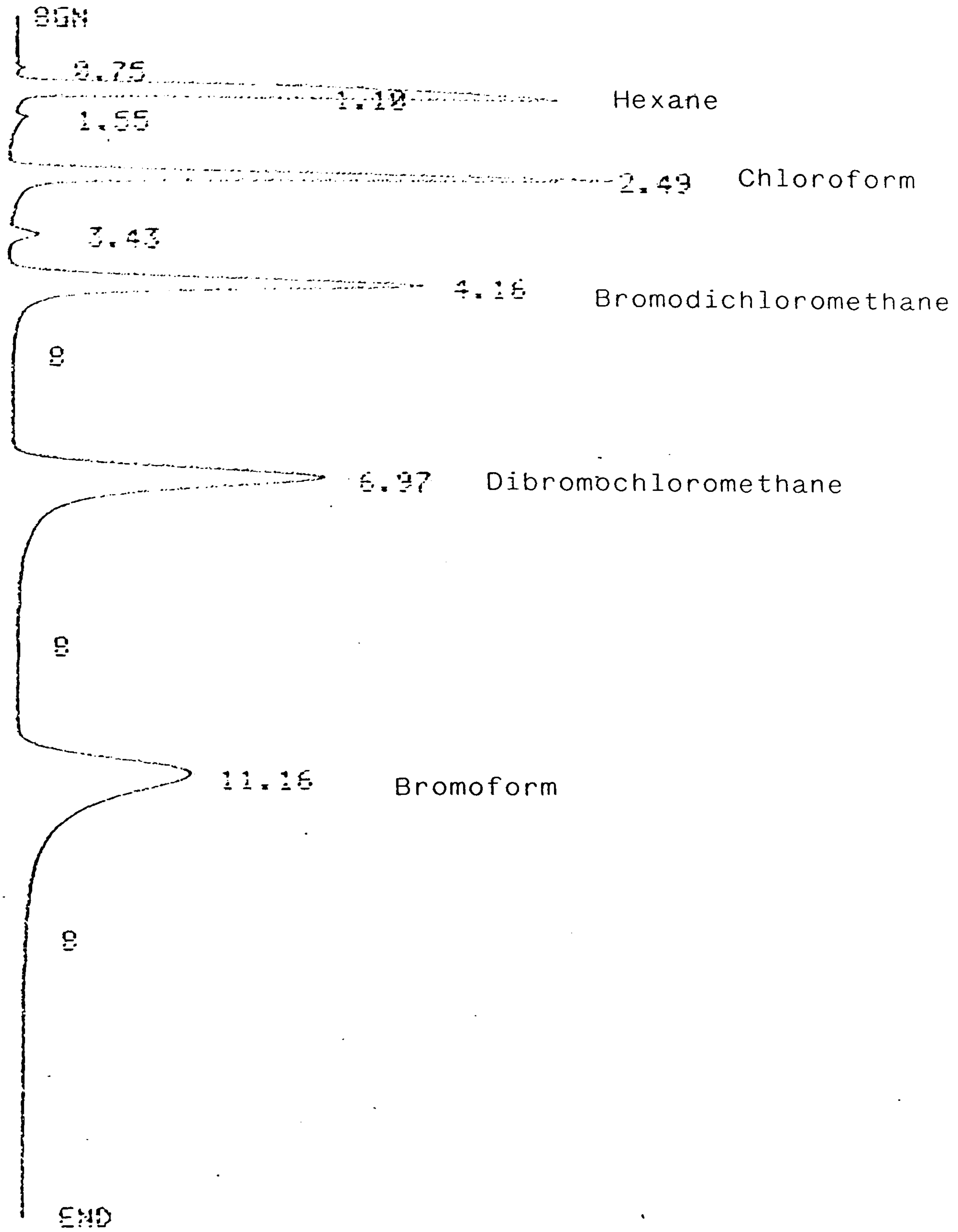
V_n/V_s- fractional recovery of organic solvent after the phase have been mixed and equilibrium is obtained.

V_n - final volume of organic solvent at equilibrium.

V_s - initial volume of organic solvent.

The *E-value*, was evaluated using the standard water solutions containing known amounts of *THM* compounds at concentrations similar to the concentrations found in water samples. Average

FIGURE 3
CHROMATOGRAM SAMPLE



Column Packing : 10% SE-30
Carrier Gas : 5% CH_4 in Argon
Carrier Flow : 60 mL/min.
Column Temperature : 55-95°C @ 2°C/min.
Detector : Electron Capture

E-values for each compound were obtained and used to calculate the concentrations of *THM* compounds in water samples. All data analysis was carried out using a personal computer utilising *LOTUS 123* spreadsheet software.

3.8 Statistical Analysis

A statistical analysis of the data generated by the analytical procedure being followed is essential in order to determine important parameters such as precision and limits of detection. Based on the data obtained in this work the following statistical parameters were determined :-

3.8.1 Precision (P)

Precision is defined as the degree of reproducibility of the results. Precision of a given analytical method can be measured by the analysis of samples in replicate. A duplicate analysis was incorporated with every set of four samples. The statistics tool measuring the precision of a duplicate analysis include the *"mean value"*, and *"range value"* and is defined as follows[336]:-

$$\boxed{P = \frac{(X_1 - X_2)\times 100}{0.5\times(X_1 + X_2)}} \qquad \text{.................. EQUATION 18}$$

where

X_1 - Maximum value

X_2 - Minimum value

The average value of the precision of each *THM* compound is given in **Table 2**. The precision of the four compounds was well within the ±20% criteria for acceptance of any analytical method[336].

3.8.2 Accuracy

Accuracy is a measure of the degree of conformity of a value generated by a specific procedure to the assumed or accepted true value, and includes both precision and bias[337]. Accuracy can be determined by measuring the percent recovery of a known addition to a sample. Samples of organic free water were spiked with a known concentration of a standard mixture containing the four *THM* compounds. The concentration of the standard mixture that was spiked was as close as possible to the concentration of the four compounds found in the samples.

Recoveries of less than 60% are usually considered unreliable due to the difficulty of obtaining the value accurately[338]. The method of standard addition, in preparing the standard, tends to lead towards erroneously low values. The lack of a homogeneous working standards containing known amounts of naturally incorporated analyte is an important limitation in modern trace organic analysis. But as reported by the **American Chemical Society** (*ACS*) Committee on Environmental Improvement[338], the measurement of field samples when corrected for recovery (less than 60%) can accurately indicate the true analyte concentration, if the accuracy and precision are established at a specified confidence limit. **Table 2** shows for each of the four compounds the accuracy which are identical with the *E-values* obtained as described earlier.

TABLE 2
QUALITY CONTROL PARAMETERS

COMPOUND	PRECISION (%)	ACCURACY (%)	STANDARD DEVIATION (µg/L)	COEFFICIENT OF VARIATION (%)	INSTRUMENT DETECTION LIMIT (µg/L)	LIMIT OF DETECTION (µg/L)
$CHCl_3$	3.78	34.32	0.12	1.53	1.490	0.35
$CHBrCl_2$	20.74	67.33	0.04	8.34	1.985	0.12
$CHBr_2Cl$	10.27	68.93	0.04	3.67	2.398	0.11
$CHBr_3$	12.25	84.06	0.15	4.73	2.912	0.46

3.8.3 Standard Deviation (SD)

The standard deviation of the four compounds, reported in **Table 2**, is calculated according to the following equation :-

$$\boxed{SD = \sqrt{\frac{(X_i - \overline{X})^2}{(n-1)}}} \quad \text{.................} \quad \textbf{EQUATION 19}$$

where

X_i - individual value

$\overline{X}$ - mean value

n - number of individual values

3.8.4 Coefficient of Variation (CV)

Coefficient of variation is defined as the precision of an overall collection of duplicate analyses, and is measured as follows :-

$$\boxed{CV = \frac{SD \times 100}{\overline{X}}} \quad \text{..................} \quad \textbf{EQUATION 20}$$

3.8.5 Instrument Detection Limit (IDL)

It is defined as the smallest signal above background noise that an instrument can detect reliably[339]. It is determined by injecting the Gas Chromatograph with a series of diluted standards until the peaks disappear. The instrument detection limit for each compound is shown in **Table 2**.

3.8.6 Limit of Detection (LOD)

Limit of detection is defined as the lowest concentration of an analyte which the analytical procedure can reliably detect[338]. This limit is measured[340], according to the following equation :-

$$\boxed{LOD = K \times SD} \quad \text{..................} \quad \textbf{EQUATION 21}$$

where

K - numerical factor chosen in accordance with the confidence level desired. A value for *K* of *3* was used which results in a confidence level of 99.86%.

The instrument detection limit and the analysis limit of detection sometimes are the same. However, by employing concentration of the samples[339], improved overall detection limits can be obtained. **Table 2** clearly illustrates this point.

CHAPTER FOUR

TRIHALOMETHANE COMPOUNDS FORMATION IN MULTI-STAGE FLASH (*MSF*) DISTILLATION PLANTS

4.1 Introduction

This chapter deals specifically with the formation of *THM* compounds during sea water desalination by utilising multi-stage flash (*MSF*) distillation plants. As a matter of fact the formation of *THM* compounds is more related to the chlorination of cooling sea water, a process which is necessary to ensure the efficient running of the distillation plant, rather than directly linked to the distillation process itself. What is of great interest, though, is the impact of the distillation process on the presence of these compounds and the final level of *THM* compounds concentration in the distilled water produced.

For this purpose, two typical and identical distillation units located at **Doha East Power Generation & Water Production Station** were chosen for the monitoring of *THM* compounds formation. The reasons for choosing these two units, apart from their representative design and capacity, is the fact that both were to be under very close surveillance as part of a performance evaluation of a new anti-scalent additive, which was to be performed during the same time the monitoring programme for this study was to be carried out. A great deal of real plant data was collected which meant that vital operational parameters were available in case they were needed.

The first aim of this chapter was to monitor the formation of *THM* compounds in cooling sea water due to the chlorination process, with respect to concentrations and types. The next step was to determine the input of *THM* compounds to the distillation plants via the make-up feed and the amount discharged back to the sea. The impact of the distillation process on *THM* compounds presence and the final concentrations of these compounds in the distilled water produced were also to be determined.

In order to link the measured *THM* compounds concentrations and the distillation plant operational parameters and to be absolutely sure about the accuracy of these concentrations, mass load analysis of these compounds employing the measured concentrations and the relevant streams volumetric flow rates was performed. Finally, to gain a close insight into the fate of *THM* compounds during the distillation process, a stage-by-stage mass load analysis of these compounds was also performed, by using suitable techniques. **Appendix I** presents the derivation of suitable sets of equations which made such analysis possible.

A preliminary analysis of the work covered by this chapter was presented at an international conference dealing with the subject of sea water desalination which was held in *Kuwait* in *1989*. The analysis presented in the paper, which was published in the conference proceedings[341], differs from the final analysis presented here in many respects.

4.2 Multi-Stage Flash (MSF) Distillation Process Description

A liquid at a given pressure has its own saturation temperature. This temperature decreases as the pressure drops. Therefore, a liquid under such saturated conditions contains the maximum amount of heat energy and will boil or vaporize, if either additional heat is supplied or the pressure is reduced.

When a liquid at saturation point is introduced into an unheated chamber in which the vapour pressure is maintained at such a level that the resident liquid is below its incoming temperature, it immediately boils or vaporizes. This phenomenon is called *"flash* *evaporation*", and a high purity distillate is then obtained by condensing this flashed vapour.

Multi-Stage Flash (*MSF*) distillation plants take full advantage of this fact to produce distilled water from sea water feed. The *MSF* evaporator is divided into a number of stages each at successively lower pressure. All stages are operated under vacuum. This vacuum is maintained by driving air ejectors. Apart from the brine heater which constitutes the heat input section, the last three stages of the evaporator constitute the heat rejection section, while the remaining stages constitute the heat gain section.

Chlorinated sea water from the intake system is circulated in the condenser tubes of the last section of the plant. The purpose of this section, which is called the heat rejection section, is to reject the heat from the distillation unit using cooling sea water. Chlorination of cooling sea water is carried out in order to prevent marine fouling of the sea water intake system and condenser tubes of the heat rejection section. The chlorination practice followed consists of both continuous dosing of 2.0 mg/L, in addition to frequent high rate shock dosing of 6.0 mg/L for short intervals which usually last for 30 minutes. Since the area where **Doha East Station** is located is shallow, the requirements of the cooling water intake system design meant that a special channel had to dredged, ending with a forebay area where chlorine gas is injected. Debris and large foreign objects are then removed from sea water by passage through stationary and travelling screens.

Most of the outlet cooling sea water, exiting the condenser tubes of the heat rejection section, is discharged back to the sea apart from a portion which is used as make-up feed and is returned back to the flash chamber of the last stage of the distillation unit. The make-up stream is deareated in a special deareation chamber after which it mixes with the brine. The deareation chamber could be either of the integral or external type. Furthermore, the integral type could be of a simple design where the deareation process is accomplished by simply spraying the make-up water on perforated plates which result, with the aid of the high vacuum existing in the last stage, in separating the dissolved oxygen or it could be of a more advanced and efficient design where pall packing and stripping steam are utilized. The deareation chamber of the distillation plants at **Doha East Station** is of the simple integral type where pall packing and stripping steam are not utilized.

Before the introduction of the make-up feed into the flash chamber of the last stage, two different chemical injections are performed. Firstly, about 1.5 - 2.5 mg/L of an anti-scalent additive is added, in order to control the formation of alkaline scale deposits such $CaCO_3$ and $Mg(OH)_2$ inside the condenser tubes, especially at the higher temperature end of the unit. The second chemical addition consists of the injection of about 0.1 mg/L of an anti-foaming agent, in order to suppress foaming tendencies of boiling concentrated sea water inside the flash chambers. Both of the above chemicals are *organic-based* compounds, which together with the organic matter present naturally in sea water form a possible precursor source for *THM* compounds formation, some of which is bound to be present in the distilled water produced.

After the feed make-up is mixed with the brine in the last stage, recirculating brine flows into the condenser tubes of the heat gain section, which in the case of the distillation plants at **Doha East Station** consists of 23 stages, where it is gradually heated by the condensing vapour in each stage condenser. The brine is finally heated to its terminal temperature by the input steam in the heat input section, after which it flows into the first stage flash chamber, where flashing occurs. The brine repeats the flashing process while passing through the inter-connected flash chambers, increasing its salts content in the process, until it reaches the last stage. A portion of the concentrated brine is then discharged as blowdown brine, in order to maintain the brine concentration within the design value. Make-up feed is then added to maintain the required mass balance.

The flashed vapour produced is salt-free, however, the violent turbulence caused by the flashing process results in droplets of brine contaminating the upward moving vapour. Therefore, a demister is positioned at the upper part of the flash chambers to intercept any such droplets and to prevent them from being carried over into the distillate tray. After the vapour passes through the demister, it comes into contact with the relatively cool tube bundles of the stage condensers, where it condenses on the tube outer surfaces and drops into the distillate tray. In the process of condensing, the vapour releases its latent heat of evaporation to the brine in the case of the heat gain section or sea water in the case of the heat rejection section flowing inside the condenser tubes. The distillate produced in each stage flows in cascade from the first stage to the last stage, where it is finally collected.

During the flashing process and due to the effect of heat, the bicarbonate ions in sea water decompose which results in the release of carbon dioxide. The distillation unit is equipped with a venting system designed to remove all gases from the unit which include oxygen released as a result of the deareation of the make-up stream and carbon dioxide liberated due to the decomposition of the bicarbonate ions.

Considering a typical distillation plant at **Doha East Station** which consists of 26 stages; 23 stages for the heat gain section and 3 stages for the heat rejection section, and under summer design conditions, the flashing brine temperature in stage No.1 is 88.7°C, while the flashing brine temperature in the last stage (*stage No. 26*), is 40.6°C. The corresponding vapour condensing temperatures are 87.5°C and 38.7°C, respectively. The flashing regime occurs under vacuum ranging from 479 mmHg in stage No.1 to 51.9 mmHg in the last stage.

Figure 4 gives the heat and mass balance diagram, while **Table 3** shows the main design characteristics of the distillation unit used for monitoring purposes in this research work, under summer design conditions. The summer design conditions, rather than the winter design conditions, are mentioned here due to the fact that they correspond more closely to the actual conditions prevalent during the monitoring of *THM* compounds formation in the distillation plant.

4.3 Monitoring Programme

The main objective of the monitoring programme was to determine the concentrations of *THM* compounds present in the distillate produced by the *MSF* sea water distillation plants utilising a polymeric anti-scalent additive. It was also designed to enable the determination of *THM* compounds concentrations and mass loads in all the distillation unit major streams.

The monitoring programme was carried out at **Doha East Power Generation & Water Production Station**, during the period between **April** and **August** *1988*. Different samples were taken at various locations within the distillation unit as shown in **Figure 4**. Five sampling points were earmarked due to their importance. The streams

FIGURE 4

HEAT AND MASS BALANCE DIAGRAM

(SUMMER DESIGN CONDITIONS)

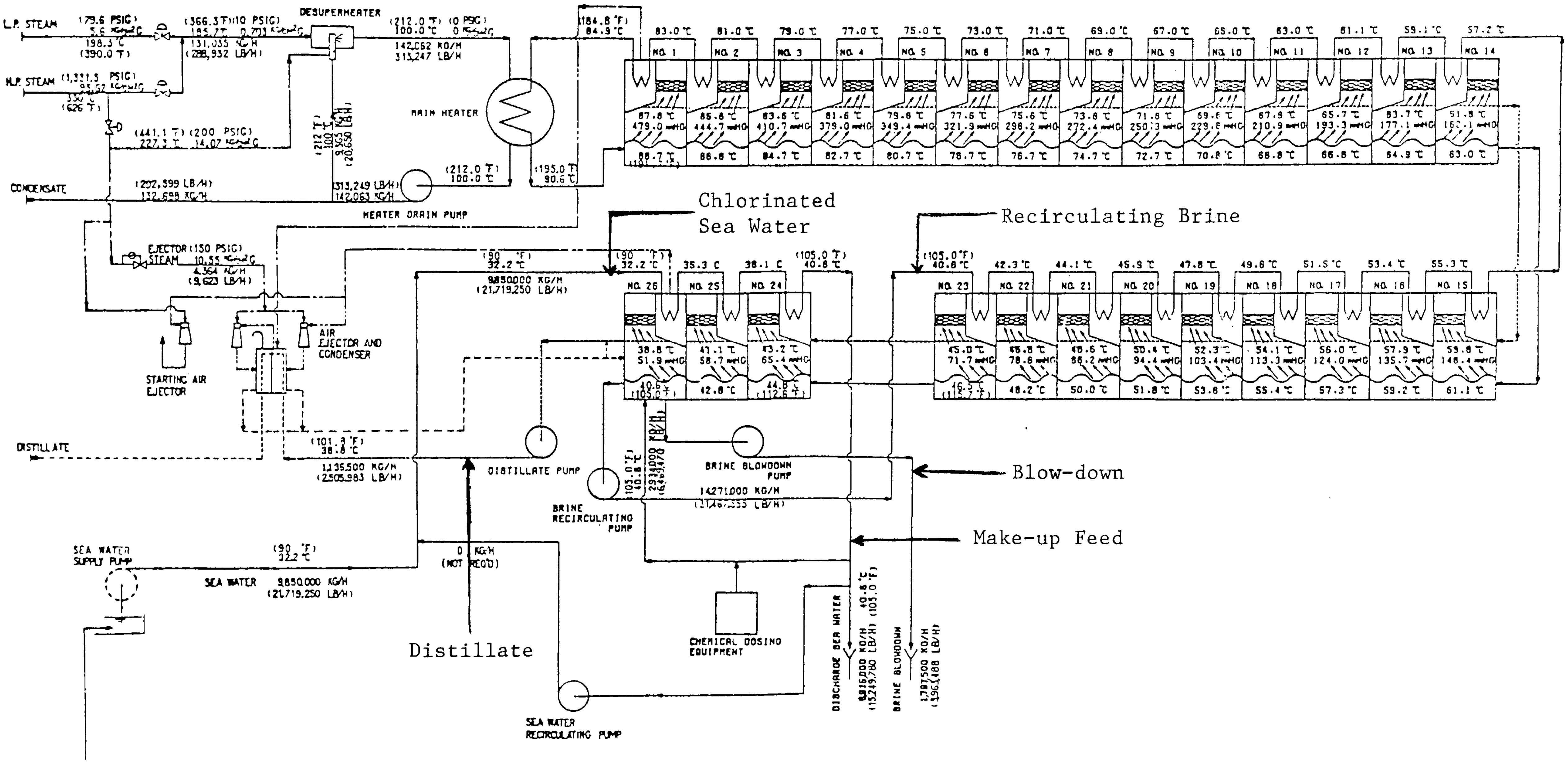


TABLE 3
DESIGN CHARACTERISTICS OF A DISTILLATION UNIT

PARAMETER	VALUE
Distillate Production	1136500 m^3 / h
Gained Output Ratio	8.00 Kg Dist./Kg Steam
Steam Consumption	282.136 KJ / Kg
Circulation Ratio	12.56
Circulating Brine Flow Rate	14271000 Kg / h
Performance Ratio	3.544 Kg / 1000 KJ
Brine Concentration Factor	1.5
Blowdown Concentration Factor	1.63
Temperature Flashing Range	50°C
Total Temperature Range	58.4°C
Steam Mass Flow Rate	142062 Kg / h
HEAT INPUT SECTION	
Fouling Factor	0.201 K m^2 / KW
Heat Transfer	89069 KJ / s
Overall Heat Transfer Coefficient	2.089 KW / m^2 K
Temperature Rise	5.7°C
HEAT GAIN SECTION	
Fouling Factor	0.147 K m^2 / KW
Heat Transfer	684248 KJ / s
Overall Heat Transfer Coefficient	2.538 KW / m^2 K
Temperature Rise	44.3°C
HEAT REJECTION SECTION	
Fouling Factor	0.183 K m^2 / KW
Heat Transfer	91374 KJ / s
Overall Heat Transfer Coefficient	2.087 KW / m^2 K
Temperature Rise	8.4°C

sampled included **chlorinated sea water** (*prior to entry to the distillation unit*), **make-up feed, recirculating brine, blowdown brine** and **distillate product**.

The data reported in this chapter is the outcome of the monitoring programme carried out, simultaneously, on two identical distillation units. Altogether, 21 data sets were collected for **A4** distillation unit, while 15 data sets were collected for **A6** distillation unit. A data set includes samples of all streams listed above. The samples collected cover both continuous and shock chlorination practices.

All process parameters which might have a bearing on the presence and formation of *THM* compounds were monitored. These include :-

a) residual chlorine level;
b) temperature;
c) *pH*;
d) anti-scalent additive dosing;
e) contact time; and
f) volumetric flow rates

4.4 THM Compounds Formation Potential During Cooling Sea Water Chlorination

In order to reject heat from the distillation unit in the heat rejection section, cooling sea water is utilised. However, before this cooling sea water is introduced to the unit, chlorination is performed at **Doha East Power Generation & Water Production Station** using free chlorine gas, in order to prevent marine biological fouling of both the distillation condenser tubes and the intake system. Both continuous and shock chlorination practices are followed, as it has been found that continuous chlorination by itself will not prevent marine biological fouling. Chlorination is carried out at the suction side of the sea water pumps some 40-60 m from the distillation units.

The potential formation of *THM* compounds will be dependent on the level of chlorine dosage which determines the level of residual chlorine present based on the chlorine demand of sea water, total organic carbon (*TOC*), *pH* of sea water, temperature of sea water, and finally contact time. As far as contact time is concerned, which is defined as the time it takes cooling sea water to travel from the intake system to the distillation unit, it is estimated to be around 0.5 minute. The *TOC* was assumed[2,342] to be in the range of 0.5-5.0 mg/L, while the *pH* of sea water was found to be around 8.20. Complete chemical analysis of sea water at **Doha Area** in **Kuwait** is given in **Table 4**.

Table 5 gives cooling sea water *THM* compounds average concentrations and mass loads values, in addition to standard deviation, maximum and minimum values for **A4** & **A6** distillation units during continuous chlorination treatment practices. The table also gives data related to the stream temperature and residual chlorine. **Table 6** gives the corresponding data for **A4** distillation unit under shock chlorination practice.

The average *TTHM* compounds concentration and mass load, for **A4** distillation unit under continuous chlorination practice, were 20.88 ± 5.64 µg/L and 187.12 ± 50.19 g/h, respectively. The corresponding values, under shock chlorination practice were 37.95 ± 6.86 µg/L and 344.04 ± 69.89 g/h, respectively. The average values for the temperature and residual chlorine level, during continuous chlorination, were 27.28 ± 1.94 °C and 0.18 ± 0.15 mg/L, respectively. While the corresponding values, during shock chlorination, were 28.47 ± 1.89 °C and 0.77 ± 1.58 mg/L, respectively.

TABLE 4
SEA WATER CHARACTERISTICS AT DOHA AREA IN KUWAIT

PARAMETER	**VALUE** (mg/L)
Sodium (Na^+)	14000
Potassium (K^+)	540
Calcium (Ca^{++})	583
Magnesium (Mg^{++})	1717
Iron (Fe^{++})	0.1
Strontium (Sr^{+++})	18
Nitrate (NO_3^-)	0.1
Sulphate (SO_4^{--})	3570
Chloride (Cl^-)	24127
Carbonate (CO_3^{--})	25
Phosphate (PO_4^{---})	0.2
Bicarbonate (HCO_3^-)	189
Fluoride (F^-)	1
Bromide (Br^-)	85
Aluminum (Al^{+++})	0.1
Silicate (SiO_2^{--})	6
Turbidity *(ntu)*	10
Oxygen (O_2)	8
Carbon Dioxide (CO_2)	2.5
pH	8.2
Total Dissolved Solids *(TDS)*	44890

TABLE 5
CHLORINATED SEA WATER THM COMPOUNDS DATA DURING CONTINUOUS CHLORINATION PRACTICE

	UNIT A4				UNIT A6			
	AVE.	STD	MAX.	MIN.	AVG.	STD	MAX.	MIN.
CONCENTRATION (µg/L)								
$CHCl_3$	0.18	0.43	1.61	0.00	0.46	0.63	1.80	0.00
$CHBrCl_2$	0.25	0.24	0.79	0.00	0.34	0.20	0.69	0.00
$CHBr_2Cl$	0.66	0.38	1.85	0.29	0.62	0.39	1.09	0.00
$CHBr_3$	19.79	5.48	28.60	8.39	22.09	11.52	38.16	2.62
TTHM	20.88	5.64	29.86	8.85	23.49	12.21	39.92	3.39
MASS LOAD (g/h)	187.12	50.19	259.20	78.18	219.03	115.93	385.89	33.63
TEMPERATURE (°C)	27.28	1.94	32.17	24.77	27.90	2.73	32.26	23.80
pH	8.77	0.06	8.90	8.65	8.71	0.05	8.80	8.60
RESIDUAL CHLORINE (mg/L)	0.18	0.15	0.50	0.01	0.10	0.13	0.50	0.00
FLOW RATE (m^3/h)	8962	413	9883	8395	9323	607	10037	7925

TABLE 6
CHLORINATED SEA WATER THM COMPOUNDS DATA DURING SHOCK CHLORINATION PRACTICE

	AVG.	STD	MAX.	MIN.
CONCENTRATION (μg/L)	**UNIT A4**			
$CHCl_3$	0.34	0.39	1.26	0.00
$CHBrCl_2$	0.55	0.33	1.23	0.17
$CHBr_2Cl$	1.15	0.23	1.68	0.91
$CHBr_3$	35.92	6.35	45.24	26.97
TTHM	37.95	6.86	48.49	28.29
MASS LOAD (g/h)	344.04	69.89	458.67	247.92
TEMPERATURE (°C)	28.47	1.89	31.15	25.85
pH	8.72	0.05	8.80	8.60
RESIDUAL CHLORINE (mg/L)	0.77	1.58	6.00	0.10
FLOW RATE (m^3/h)	9064	358	9612	8666

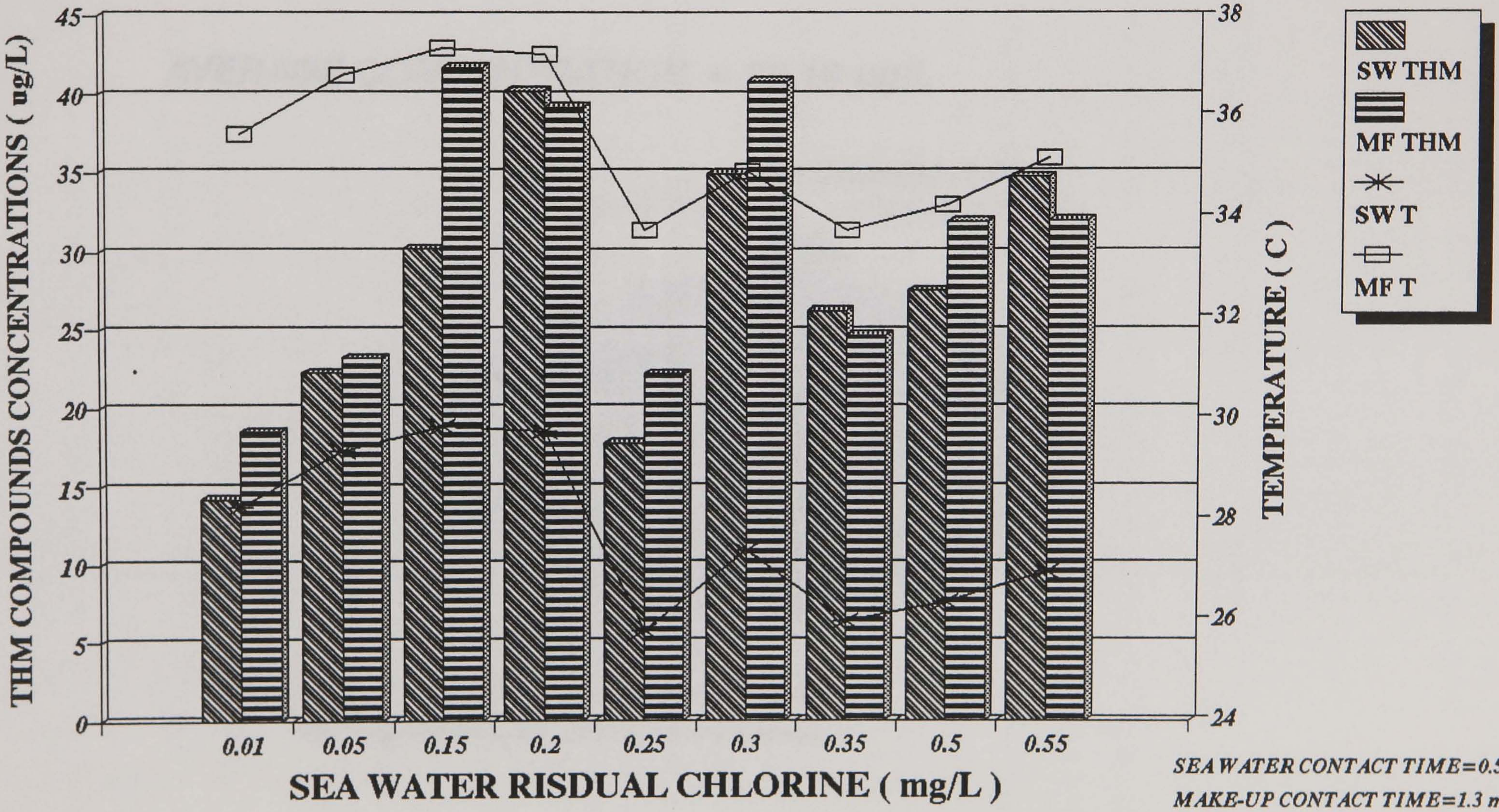
As far as **A6** distillation unit is concerned, the *TTHM* compounds average concentration and mass load, during continuous chlorination practice, were 23.49 ± 12.21 µg/L and 219.03 ± 115.93 g/h, respectively. The average values for the stream temperature and level of residual chlorine, during continuous chlorination, were 27.90 ± 2.73°C and 0.10 ± 0.13 mg/L, respectively. The effect of chlorination practice, whether continuous or shock, is clearly evident. The potential for *THM* compounds formation is greatly enhanced during shock chlorination due to higher available chlorine for *THM* compound formation reactions. The level of enhancement is dependent on chlorine dose and duration of shock treatment.

Figure 5 clearly shows the effect of both the level of residual chlorine and the temperature of cooling sea water on the concentration of *TTHM* compounds. The two parameters have a combined effect on *THM* compounds formation. Assuming a constant chlorine demand, it is evident that *TTHM* compounds concentrations increase steadily with increasing levels of residual chlorine, especially when the stream temperature is increasing. However, *THM* compounds formation is dampened when the temperature is decreasing. It was possible to determine that the potential for *THM* compounds formation increases linearly with increasing levels of residual chlorine, i.e. chlorine dosage and increases exponentially with increasing temperature.

The dominance of bromoform ($CHBr_3$), under both continuous and shock chlorination practices and for both **A4** and **A6** distillation units, was clearly demonstrated. **Figure 6** illustrates the relative distribution of the *THM* compounds in cooling sea water stream based on the average concentrations of these compounds obtained from the monitoring of the two distillation units under continuous chlorination practice. Bromoform constitutes about 94% of the total *THM* compounds formed. This trend was observed in all samples and under

FIGURE 5
CHLORINATION & TEMPERATURE IMPACT

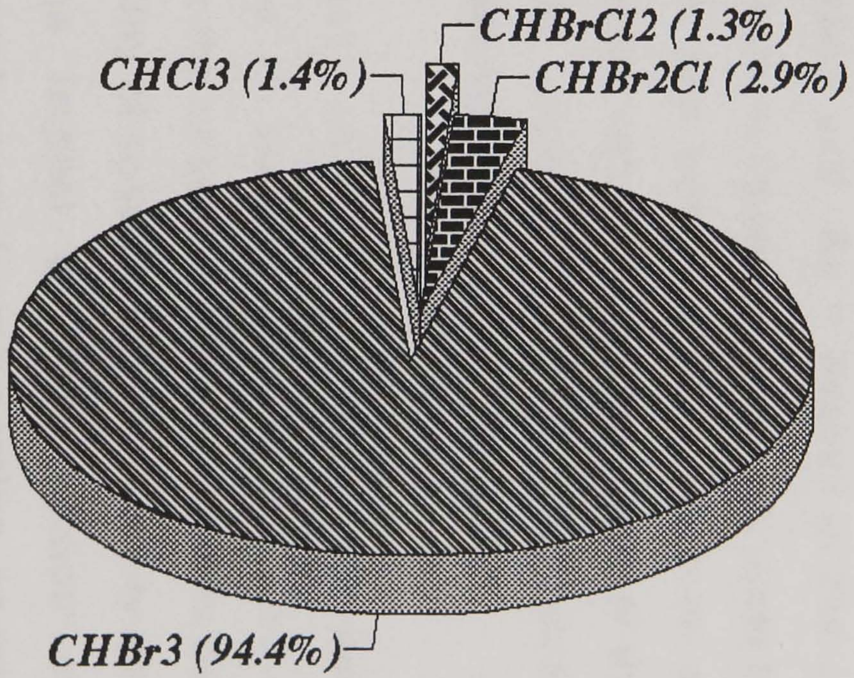
ON THM COMPOUNDS FORMATION



SEA WATER CONTACT TIME=0.5min.
MAKE-UP CONTACT TIME=1.3 min.

FIGURE 6
SEAWATER THM COMPOUNDS DISTRIBUTION

AVERAGE CONCENTRATION = 22.19 ug/L



RESIDUAL CHLORINE = 0.14 mg/L, TOC = 0.5 - 5.0 mg/L,
TEMPERATURE = 27.59 C, CONTACT TIME = 0.5 min.

varied conditions of residual chlorine levels and stream temperatures. This dominance is expected[11,12,123] and is due to the rather high concentration (75.0 ± 0.25 mg Br^-/L) of bromide ion present in sea water in **Kuwait**[2] .

4.5 Distillation Unit THM Compounds Input

The above *THM* compounds formation in cooling sea water stream is prior to entry to the distillation unit. As it passes in the condenser tubes of the heat rejection section, its temperature increases as it acts as a cooling medium. Upon exit from the heat rejection section, a certain portion of the flow which constitutes about 30% of the total, is used as make-up feed to be introduced to the distillation unit last stage flash chamber after deareation.

The make-up feed is, therefore, characterized by higher temperature, lower residual chlorine due to further consumption and increased contact time. No changes in the chemistry of sea water is expected to occur, although, the possibility of some biological activity could not be ruled out completely. The impact of any addition of organic compounds, such as anti-scalent and anti-foaming agents will not manifest itself here, as the sampling point for the make-up feed stream is prior to such an addition.

Table 7 gives make-up feed *THM* compounds average concentrations and mass load values, in addition to standard deviation, maximum and minimum values for **A4** & **A6** distillation units during continuous chlorination practice. The table also gives data related to the stream temperature and residual chlorine. **Table 8** gives the corresponding data for **A4** distillation unit during shock chlorination practice. Only one sample was collected for the make-up stream in the case of **A6**

TABLE 7
MAKE - UP FEED THM COMPOUNDS DATA DURING CONTINUOUS CHLORINATION PRACTICE

	UNIT A4				UNIT A6			
	AVG.	**STD**	**MAX.**	**MIN.**	**AVG.**	**STD**	**MAX.**	**MIN.**
CONCENTRATION (µg/L)								
$CHCl_3$	0.54	1.34	5.01	0.00	0.84	1.25	4.56	0.00
$CHBrCl_2$	0.37	0.40	1.51	0.00	0.23	0.20	0.58	0.00
$CHBr_2Cl$	0.68	0.27	1.40	0.34	0.62	0.43	1.25	0.00
$CHBr_3$	21.20	6.26	29.45	7.62	24.29	12.17	45.51	4.09
TTHM	22.78	6.68	35.15	8.40	25.98	12.72	49.02	4.44
MASS LOAD (g/h)	65.07	19.42	99.39	24.20	73.17	35.60	135.10	12.35
TEMPERATURE (°C)	34.85	1.70	39.08	32.53	35.65	2.30	39.80	32.96
pH	8.74	0.04	8.80	8.63	8.70	0.04	8.75	8.60
RESIDUAL CHLORINE (mg/L)	0.12	0.11	0.30	0.01	0.07	0.07	0.25	0.00
FLOW RATE (m^3/h)	2856.60	90.07	3056.18	2706.25	2817.02	70.15	2978.33	2748.75

TABLE 8
MAKE-UP FEED THM COMPOUNDS DATA DURING SHOCK CHLORINATION PRACTICE

	AVG.	STD	MAX.	MIN.
CONCENTRATION (μg/L)	**UNIT A4**			
$CHCl_3$	0.31	0.40	1.23	0.00
$CHBrCl_2$	0.55	0.49	1.51	0.00
$CHBr_2Cl$	1.24	0.42	2.03	0.59
$CHBr_3$	39.53	11.06	61.67	21.74
TTHM	41.63	11.90	65.71	22.58
MASS LOAD (g/h)	121.88	35.17	197.99	66.24
TEMPERATURE (°C)	36.14	1.83	38.75	33.14
pH	8.72	0.04	8.80	8.68
RESIDUAL CHLORINE (mg/L)	0.66	1.54	5.50	0.01
FLOW RATE (m^3/h)	2927	80	3044	2757

distillation unit during shock chlorination practice.

The average total trihalomethane (*TTHM*) compounds concentration and mass load were 22.78 ± 6.68 µg/L and 65.07 ± 19.42 g/h, respectively, for **A4** distillation unit under continuous chlorination practice. The corresponding values, under shock chlorination practice were 41.63 ± 11.90 µg/L and 121.88 ± 35.17 g/h, respectively. The average values for the temperature and residual chlorine level, during continuous chlorination, were 34.85 ± 1.70 °C and 0.12 ± 0.11 mg/L, respectively, while the corresponding values, during shock chlorination, were 36.14 ± 1.83 °C and 0.66 ± 1.54 mg/L, respectively.

As far as **A6** distillation unit is concerned, the *TTHM* compounds average concentration and mass load, during continuous chlorination practice, were 25.98 ± 12.72 µg/L and 73.17 ± 35.60 g/h, respectively. During shock chlorination practice, the corresponding values for the *TTHM* concentration and mass load were 65.32 µg/L and 179.40 g/h, respectively. The average values for the stream temperature and level of residual chlorine, during continuous chlorination, were 35.65 ± 2.30 °C and 0.07 ± 0.07 mg/L, respectively, while the corresponding values, during shock chlorination, were 36.27 °C and 0.37 mg/L, respectively.

It is clear that *THM* compounds concentrations in the make-up feed stream are slightly higher than their concentrations in chlorinated sea water stream prior to entry to the distillation unit. This is explained by increased contact time and higher temperature. It is estimated that the contact time for the make-up feed stream at sampling point is 1.3 minute compared to 0.5 minute for chlorinated sea water at its sampling point. Furthermore, on average the temperature of make-up stream is about 7.6 °C higher than that of sea water. **Figure 5** clearly shows this trend.

It can be estimated from the monitoring of **A4** distillation unit that the volume of make-up feed flow utilised constituted between 33.77% and 27.38% with a mean value of 31.94% of the original volume of cooling sea water entering the unit. At the same time, and based on *THM* compounds mass loads, make-up stream contained between 57.23% and 21.72% with an average value of 35.54% of the *THM* compounds originally present in the cooling water entering the distillation unit. A similar corresponding trend was observed in the case of **A6** distillation unit. This proves that further *THM* compounds formation occurs during the passage of sea water in the condenser tubes of the heat rejection section. It should be remembered that the sampling point for the make-up stream is prior to the addition of the anti-scalent and anti-foaming additives. Based on the above analysis, it is estimated that on average 133.96 g/h during continuous chlorination and 300.93 g/h during shock chlorination of *THM* compounds are discharged back to the sea from a distillation unit with a production capacity of 27276 m^3/day (6.0 MIGPD), requiring cooling sea water flow rate of about 9200 m^3/h.

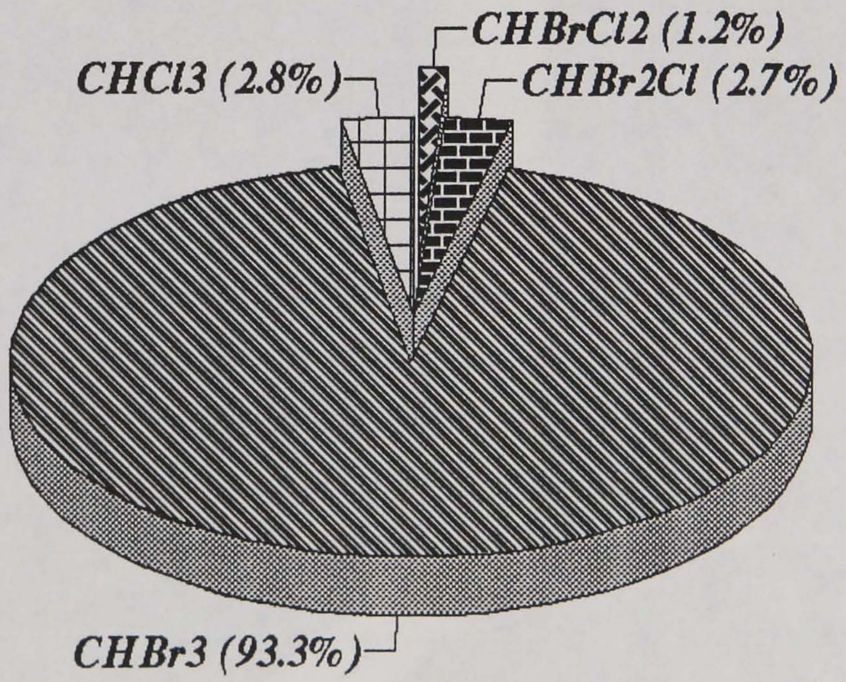
Figure 7 shows the continued dominance of bromoform in the make-up feed stream constituting about 93% of the *TTHM* concentration present. The other feature is the relative increase in chloroform concentration as compared to that detected in sea water. A comparison of the *THM* compounds concentration between sea water and make-up streams is illustrated in **Figure 8**.

4.6 Distillate Product THM Compounds Concentrations

The make-up feed stream, after addition of both the anti-scalent and the anti-foaming chemicals, is then introduced to the last stage of the distillation unit, where it is deareated and mixed with the brine left in

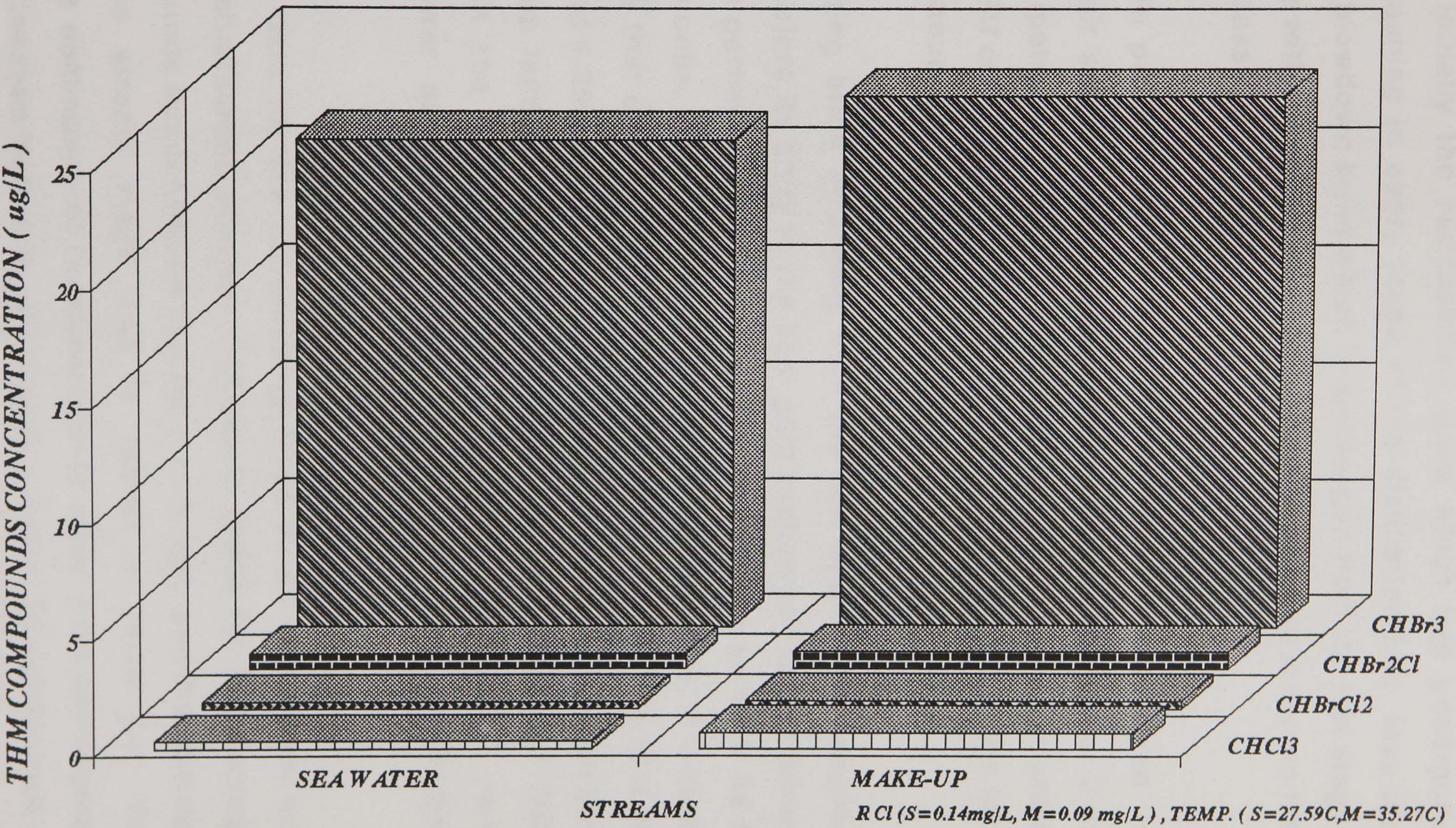
FIGURE 7
MAKE-UP THM COMPOUNDS DISTRIBUTION

AVERAGE CONCENTRATION = 24.38 ug/L



RESIDUAL CHLORINE = 0.09 mg/L , TOC = 0.5 - 5.0 mg/L
TEMPERATURE = 35.27 C , CONTACT TIME = 1.3 min.

FIGURE 8
THM COMPOUNDS DISTRIBUTION



R Cl (S=0.14mg/L, M=0.09 mg/L) , TEMP. (S=27.59C,M=35.27C)
CONTACT TIME (S=0.5 min.,M=1.3 min.)

the stage, to produce the recirculating brine. The brine residing in the last stage is initially the recirculating brine which had undergone consecutive flashing in every stage of the distillation unit, less the amount of the blowdown brine which is discharged from the last stage, prior to mixing with the make-up feed stream, in order to maintain the required salt passage.

The deareation process, in the distillation unit being monitored, is basically an air stripping operation under vacuum conditions. It is strongly anticipated that the deareation process will result in some removal of *THM* compounds from the make-up feed stream in the last stage. This amount will be quantified later.

The recirculating brine emerging from the last stage was sampled immediately before its entry to the heat gain section condenser tubes. **Table 9** gives pertinent data for the recirculating brine for both **A4** & **A6** distillation units, under continuous chlorination practice. It is clear from the table that although *TTHM* compounds concentration at 4.48 ± 1.46 µg/L and 4.29 ± 2.18 µg/L, respectively, is much lower than that of the make-up feed stream in both cases, the mass loads of *THM* compounds in the recirculating brine of both units, were only marginally lower at 58.90 ± 18.78 g/h and 58.25 ± 29.08 g/h, respectively.

The relevant data for the recirculating brine in **A4** distillation unit under shock chlorination practice is shown in **Table 10**. The average *TTHM* compounds concentration is 8.02 ± 1.79 µg/L and the average value for the stream mass load is 106.61 ± 24.24 g/h. The overwhelming dominance of bromoform over other *THM* compounds, which was witnessed before is still clearly evident. The difference in the mass loads of the make-up feed and recirculating brine streams must be due to the removal of *THM* compounds from the make-up feed

TABLE 9
RECIRCULATING BRINE THM COMPOUNDS DATA DURING CONTINUOUS CHLORINATION PRACTICE

	UNIT A4				UNIT A6			
	AVG.	STD	MAX.	MIN.	AVG.	STD	MAX.	MIN.
CONCENTRATION (µg/L)								
$CHLCl_3$	0.08	0.21	0.71	0.00	0.15	0.48	1.39	0.00
$CHBrCl_2$	0.07	0.07	0.25	0.00	0.03	0.08	0.21	0.00
$CHBr_2Cl$	0.11	0.09	0.28	0.00	0.11	0.14	0.43	0.00
$CHBr_3$	4.22	1.48	6.63	1.45	4.00	1.99	7.30	0.57
TTHM	4.48	1.46	6.84	1.70	4.29	2.18	7.53	0.74
MASS LOAD (g/h)	58.90	18.78	89.25	22.81	58.25	29.08	96.33	10.19
pH	8.85	0.07	8.95	8.70	8.70	0.04	8.75	8.60
RESIDUAL CHLORINE (mg/L)	0.01	0.01	0.04	0.00	0.01	0.02	0.05	0.00
FLOW RATE (m^3/h)	13142	259	13758	12834	13577	396	13916	12679

TABLE 10
RECIRCULATING BRINE THM COMPOUNDS DATA DURING SHOCK CHLORINATION PRACTICE

	AVG.	STD	MAX.	MIN.
CONCENTRATION (µg/L)	**UNIT A4**			
$CHCl_3$	0.07	0.17	0.56	0.00
$CHBrCl_2$	0.12	0.11	0.34	0.00
$CHBr_2Cl$	0.23	0.09	0.41	0.13
$CHBr_3$	7.67	1.71	11.09	4.79
TTHM	8.02	1.79	11.59	4.97
MASS LOAD (g/h)	106.61	24.24	157.36	66.24
pH	8.80	0.05	8.85	8.70
RESIDUAL CHLORINE (mg/L)	0.02	0.02	0.05	0.01
FLOW RATE (m^3/h)	13295	190	13576	12780

stream by the deareation process. By comparing the *TTHM* compounds average mass load values of the make-up feed and recirculating brine under both continuous and shock chlorination practices, it is possible to show that percentage compounds removal due to deareation under both cases were similar.

The next stream to be analysed was the blowdown brine which is rejected from the last stage. Although, very small concentrations of *THM* compounds were detected, they were below the statistically determined detection limits. Therefore, these concentrations were not considered of any significance and, thus, it was reasonable to assume that the blowdown brine stream contained no *THM* compounds at all.

The final stream to be analysed is the distillate product. **Table 11** shows the relevant data for both **A4** & **A6** distillation units, under continuous chlorination practice. The *TTHM* compounds average concentrations were 3.39 ± 1.42 µg/L and 2.70 ± 1.15 µg/L, while the *TTHM* compounds average mass loads were 3.86 ± 1.60 g/h and 3.05 ± 1.29 g/h, respectively. When compared to the *TTHM* compounds mass load input to both distillation units via the make-up feed stream, the *TTHM* compounds mass load in the distillate product of both units represent only 6.08% and 4.39%, respectively.

Table 12 gives similar data related to distillate product of **A4** distillation unit under shock chlorination practice. The average *TTHM* compounds concentration in the distillate is now higher at 7.89 ± 5.43 µg/L, while the mass load is 9.01 ± 6.31 g/h. This represents only 7.68% of the original *TTHM* compounds mass load in the make-up feed stream of the distillation unit.

It is clear from the data contained in the above tables that the dominance of bromoform has slightly decreased to around 87%. The

TABLE 11
DISTILLATE THM COMPOUNDS DATA DURING CONTINUOUS CHLORINATION PRACTICE

	UNIT A4				UNIT A6			
	AVG.	STD	MAX.	MIN.	AVG.	STD	MAX.	MIN.
CONCENTRATION (µg/L)								
$CHCl_3$	0.00	0.18	0.54	0.00	0.00	0.22	0.53	0.00
$CHBrCl_2$	0.47	0.22	0.78	0.00	0.28	0.23	0.83	0.00
$CHBr_2Cl$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$CHBr_3$	2.92	1.33	5.21	0.82	2.42	1.04	4.23	0.46
TTHM	3.39	1.42	5.82	1.34	2.70	1.15	5.05	0.54
MASS LOAD (g/h)	3.86	1.60	6.58	1.57	3.05	1.29	5.57	0.62
RESIDUAL CHLORINE (mg/L)	0.01	0.01	0.03	0.00	0.01	0.02	0.05	0.00
FLOW RATE (m^3/h)	1136	22	1174	1093	1128	24	1166	1094

TABLE 12
DISTILLATE THM COMPOUNDS DATA DURING SHOCK CHLORINATION PRACTICE

	AVG.	STD	MAX.	MIN.
CONCENTRATION (µg/L)	**UNIT A4**			
$CHCl_3$	0.00	0.58	2.10	0.00
$CHBrCl_2$	0.74	0.19	1.06	0.34
$CHBr_2Cl$	0.11	0.12	0.32	0.00
$CHBr_3$	7.04	5.48	19.02	2.13
TTHM	7.89	5.43	20.16	2.83
MASS LOAD (g/h)	9.01	6.31	23.40	3.17
RESIDUAL CHLORINE (mg/L)	0.03	0.04	0.10	0.01
FLOW RATE (m^3/h)	1142	11	1160	1119

other important feature is the relatively high concentration of bromodichloromethane (*$CHBrCl_2$*) present in the distillate. **Figure 9** shows the average relative distribution of *THM* compounds in the distillate.

4.7 Overall THM Compounds Formation Potential

Based on the monitoring programme carried out on both **A4** & **A6** distillation units, an overall picture could be drawn concerning *THM* compounds formation potential in a typical multi-stage flash distillation plant.

Table 13 lists the average values of the measured concentrations of the *THM* compounds in the streams sampled, which include cooling sea water, make-up feed, recirculating brine and distillate, under continuous chlorination practice. The table also lists other data which is of relevance to the concentrations of *THM* compounds in each stream. No data appears for the blowdown brine as it was deduced from the very low concentrations obtained for this stream and the analytical procedure statistical detection limits that the actual *THM* compounds concentrations in the blowdown brine should be taken to be nil.

This was not the case under shock chlorination practice, where the concentrations of the *THM* compounds were above the analytical procedure detection limits. **Table 14** lists the concentrations of the *THM* compounds in all streams sampled, for **A4** distillation unit. A definite increase in the concentrations of all streams can be observed.

By utilising the measured concentrations of the *THM* compounds and the relevant streams volumetric flow rates, the mass loads of the *THM*

FIGURE 9
DISTILLATE THM COMPOUNDS DISTRIBUTION

AVERAGE CONCENTRATION = 3.05 ug/L

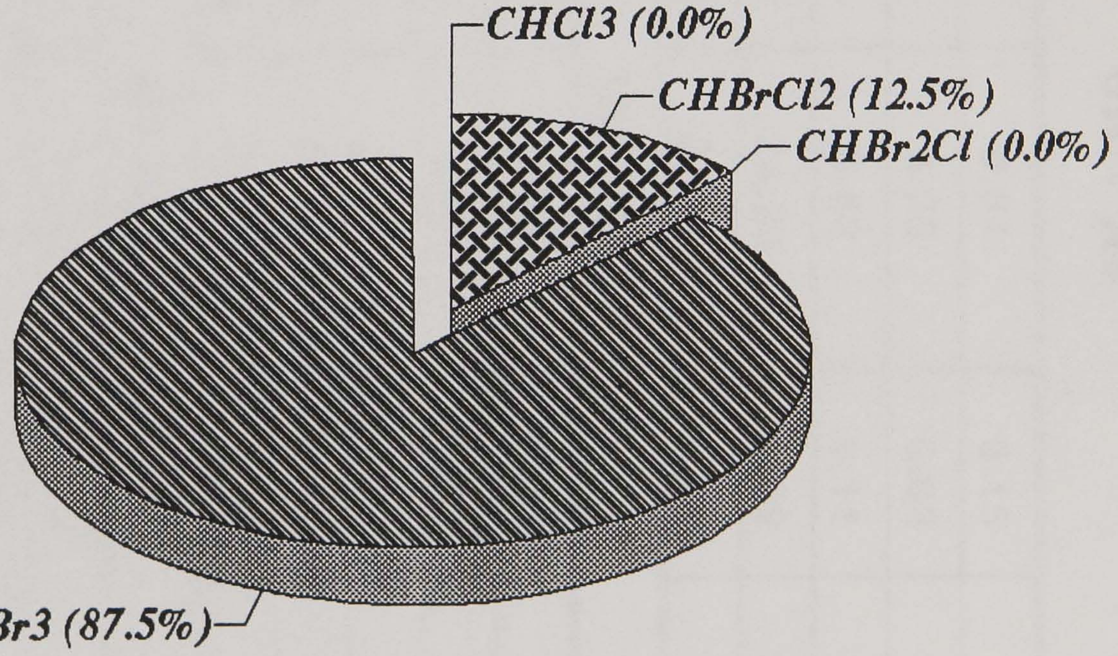


TABLE 13
OVERALL AVERAGE CONCENTRATION OF THM COMPOUNDS DURING CONTINUOUS CHLORINATION PRACTICE

	SEA WATER	MAKE-UP	BRINE	DISTILLATE
CONCENTRATION (µg/L)	**UNIT A6**			
$CHCl_3$	0.46	0.84	0.15	0.00
$CHBrCl_2$	0.34	0.23	0.03	0.28
$CHBr_2Cl$	0.62	0.62	0.11	0.00
$CHBr_3$	22.09	24.29	4.00	2.42
TTHM	23.49	25.98	4.29	2.70
UNIT A4				
$CHCl_3$	0.18	0.54	0.08	0.00
$CHBrCl_2$	0.25	0.37	0.07	0.47
$CHBr_2Cl$	0.66	0.68	0.11	0.00
$CHBr_3$	19.79	21.20	4.22	2.92
TTHM	20.88	22.78	4.48	3.39
OVERALL				
$CHCl_3$	0.32	0.69	0.12	0.00
$CHBrCl_2$	0.29	0.30	0.05	0.38
$CHBr_2Cl$	0.64	0.65	0.11	0.00
$CHBr_3$	20.94	22.74	4.11	2.67
TTHM	22.19	24.38	4.39	3.05
TEMPERATURE (°C)	27.59	35.27		
RESIDUAL CHLORINE (mg/L)	0.14	0.09		
CONTACT TIME (min.)	0.94	1.84		

TABLE 14
OVERALL AVERAGE CONCENTRATION OF THM COMPOUNDS DURING SHOCK CHLORINATION PRACTICE

	SEA WATER	MAKE-UP	BRINE	DISTILLATE	BLOWDOWN
CONCENTRATION (µg/L)	**UNIT A6**				
$CHCl_3$	1.96	2.26	0.06	0.18	0.04
$CHCl_2Br$	1.19	1.52	0.21	0.48	0.05
$CHClBr_2$	2.32	1.94	0.34	0.28	0.08
$CHBr_3$	65.03	59.60	12.25	7.71	1.97
TTHM	70.49	65.32	12.86	8.65	2.13
UNIT A4					
$CHCl_3$	0.34	0.31	0.07	0.00	0.00
$CHCl_2Br$	0.55	0.55	0.12	0.74	0.00
$CHClBr_2$	1.15	1.24	0.23	0.11	0.00
$CHBr_3$	35.92	39.53	7.67	7.04	0.00
TTHM	37.95	41.63	8.02	7.89	0.00
OVERALL					
$CHCl_3$	1.15	1.28	0.03	0.09	0.02
$CHCl_2Br$	0.87	1.04	0.16	0.61	0.02
$CHClBr_2$	1.73	1.59	0.29	0.20	0.04
$CHBr_3$	50.47	49.57	9.96	7.38	0.98
TTHM	54.22	53.48	10.44	8.27	1.06

compounds in each sampled stream can be determined. Furthermore, by establishing appropriate *THM* compounds mass balances on the distillation unit, the mass loads of *THM* compounds in the vent gases can be calculated. The vent gases consist of gases (*mostly carbon dioxide*) that are rejected from each stage during flashing and other gases (*mostly oxygen*) which are rejected in the deareation chamber attached to the last stage. It should be realized here that *THM* compounds concentrations were not analytically measured in the vent gases due to difficulty in obtaining representative samples and the associated problem of estimating the flow rate of vent gases required for relating the measured concentrations to the corresponding mass loads.

The mass loads of *THM* compounds in the gases which are released during flashing and which are sucked by the vent system can be calculated from the mass loads of the recirculating brine, distillate product and the flashing brine streams. The above mass loads are obtained using the above streams measured *THM* compounds concentrations and their corresponding volumetric flow rates.

A basic assumption in all the following analysis is that there is no destruction or conversion of *THM* compounds during the distillation process. This means that *THM* compounds mass loads input to the distillation unit must equal their corresponding output mass loads. Therefore :-

$$m_m = m_d + m_{bd} + m_{vg} \qquad \text{Eq. 22}$$

In addition *THM* compounds mass loads before and after flashing must be equal. Therefore, the mass loads of *THM* compounds in the recirculating brine must be equal to the summation of the mass loads of *THM* compounds in the distillate, vent gases from stages and the flashing brine left in the last stage. Therefore :-

$$m_r = m_d + m_g + m_f \qquad \text{Eq. 23}$$

Thus,

$$m_g = m_r - m_d - m_f \qquad \text{Eq. 24}$$

Next by establishing a mass balance of *THM* compounds mass loads in the last stage of the distillation unit, the mass loads of *THM* compounds in the deareation gases can be calculated. Again by assuming that there is no destruction or conversion of *THM* compounds, input and output mass loads of *THM* compounds of the last stage must be equal. Therefore :-

$$m_m + m_f = m_r + m_{de} + m_{bd} \qquad \text{Eq. 25}$$

By substituting *Eq.23* in *Eq.25* , we get

$$m_{de} = m_m - m_d - m_g - m_{bd} \qquad \text{Eq. 26}$$

The *THM* compounds total mass loads of the vent gases is, thus, equal to the summation of the mass loads of the gases released in the stages and the mass loads of the deareation gases. Thus:

$$m_{vg} = m_g + m_{de} \qquad \text{Eq. 27}$$

By utilising the above equations to establish the required *THM* compounds mass balances, it was possible to obtain the overall picture regarding *THM* compounds mass loads in every stream of the distillation unit. The data shown in **Table 15** represents average values obtained from both distillation units under continuous

TABLE 15
OVERALL AVERAGE MASS LOADS OF THM COMPOUNDS DURING CONTINUOUS CHLORINATION PRACTICE

MASS LOADS (g/h)	SEA WATER	MAKE-UP	BRINE	DISTILLATE
	UNIT A6			
$CHCl_3$	4.25	2.37	2.04	0.00
$CHBrCl_2$	3.13	0.64	0.41	0.32
$CHBr_2Cl$	5.74	1.74	1.49	0.00
$CHBr_3$	205.91	68.42	54.31	2.73
TTHM	219.03	73.17	58.25	3.05
	UNIT A4			
$CHCl_3$	1.60	1.54	1.09	0.00
$CHBrCl_2$	2.24	1.05	0.92	0.53
$CHBr_2Cl$	5.88	1.94	1.45	0.00
$CHBr_3$	177.40	60.55	55.45	3.32
TTHM	187.12	65.07	58.90	3.86
	OVERALL			
$CHCl_3$	2.92	1.96	1.56	0.00
$CHBrCl_2$	2.69	0.84	0.66	0.43
$CHBr_2Cl$	5.81	1.84	1.47	0.00
$CHBr_3$	191.65	64.48	54.88	3.03
TTHM	203.08	69.12	58.58	3.45

chlorination practice. **Table 16** indicates that *TTHM* compounds mass load of 203.08 g/h is generated during continuous chlorination of cooling sea water. Out of this 69.12 g/h is introduced to the distillation unit via the make-up feed stream, representing 34.04% of the total present in cooling sea water. This means that the remaining mass load of 133.96 g/h, representing 65.96%, is discharged back to sea. **Figure 10** illustrates the fate of *THM* compounds formed during the chlorination of sea water.

Table 16 also shows that the vast majority of the mass loads of *THM* compounds in the make-up stream is rejected from the distillation unit via the vent system. Total mass load in the vent gases is 65.67 g/h, of which 55.12 g/h, representing 83.93%, is contained in the gases removed from the stages and 10.55 g/h, representing 16.07%, is contained in the gases removed by the deareation process.

By comparing the above mass loads with *THM* compounds mass loads in the make-up feed stream, it is can be demonstrated that the distillation process removes 95.00% of any *THM* compounds that might be present in the make-up feed, with the remaining 5.00% being condensed along with the distillate product as shown in **Figure 11**.

After determining the *THM* compounds mass loads in all distillation unit streams, it is possible to draw an overall picture. **Figure 12** shows the mass load of each *THM* compounds in all relevant streams.

4.8 Stage-by-Stage THM Compounds Flashing-Condensing Behaviour in the Distillation Unit

The overall picture outlined above is based on data obtained through analytical measurements and, in the case of the vent gases, by carrying

TABLE 16

OVERALL THM COMPOUNDS MASS LOADS IN DIFFERENT STREAMS OF THE DISTILLATION UNIT DURING CONTINUOUS CHLORINATION PRACTICE

PARAMETER	MASS LOAD (g/h)	PERCENTAGE (%)
CHLORINATED SEA WATER	203.08	100
MAKE-UP FEED INTAKE	69.12	34.04
DISCHARGED SEA WATER	133.96	65.96
DEAREATION GASES	10.55	15.26[*]
DISTILLATE PRODUCT	3.45	4.99[*] 1.69[**]
TOTAL VENT GASES	65.67	95.01

*with respect to THM compounds mass loads in make-up feed stream

**with respect to THM compounds mass loads in sea water stream

FIGURE 10

SEAWATER THM COMPOUNDS FATE

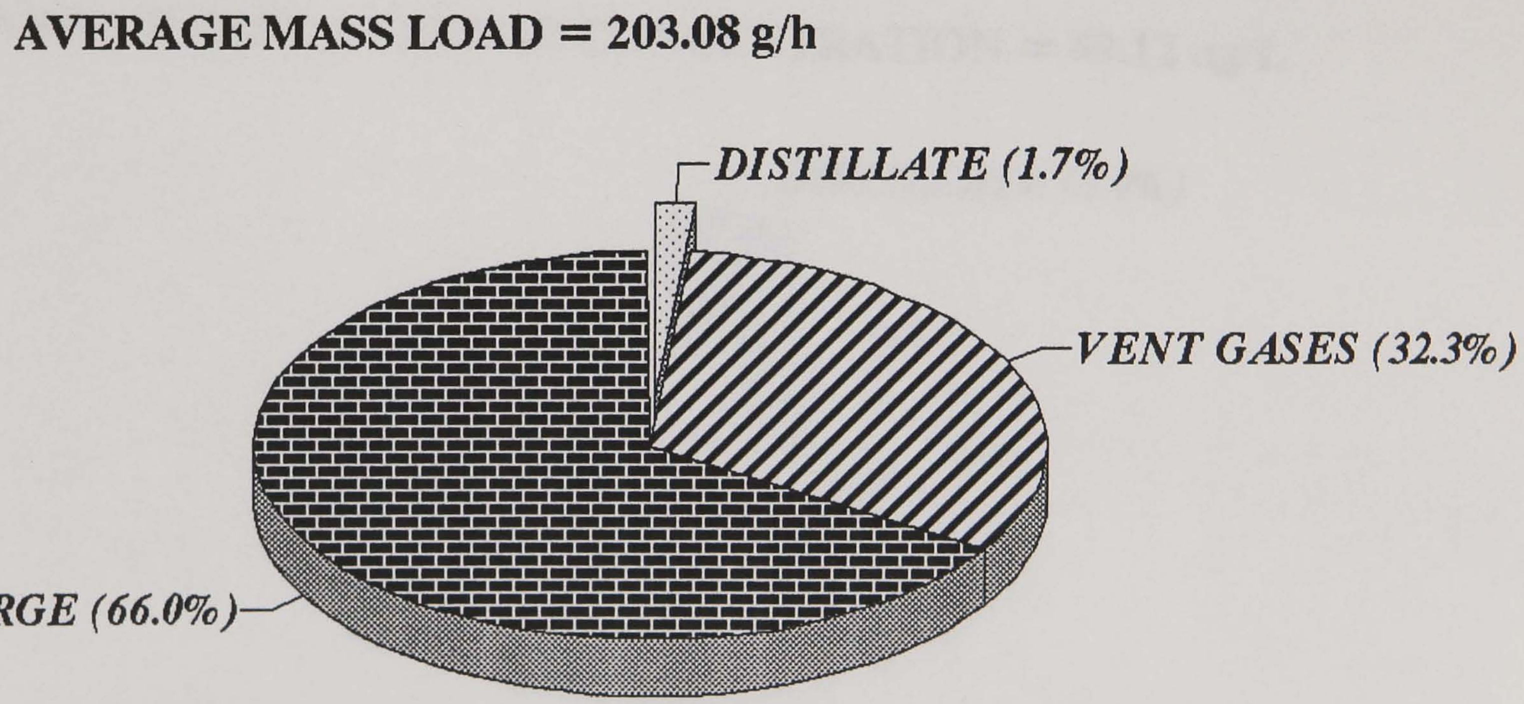


FIGURE 11
THM COMPOUNDS REMOVAL EFFICIENCY

MAKE-UP FEED AVERAGE CONCENTRATION = 69.12 ug/L

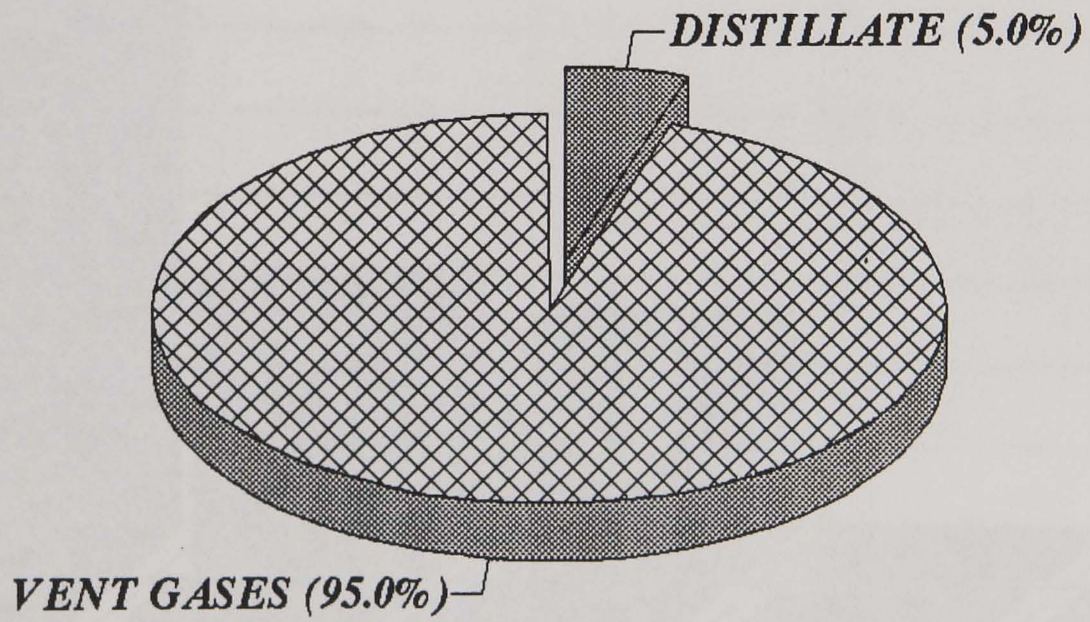
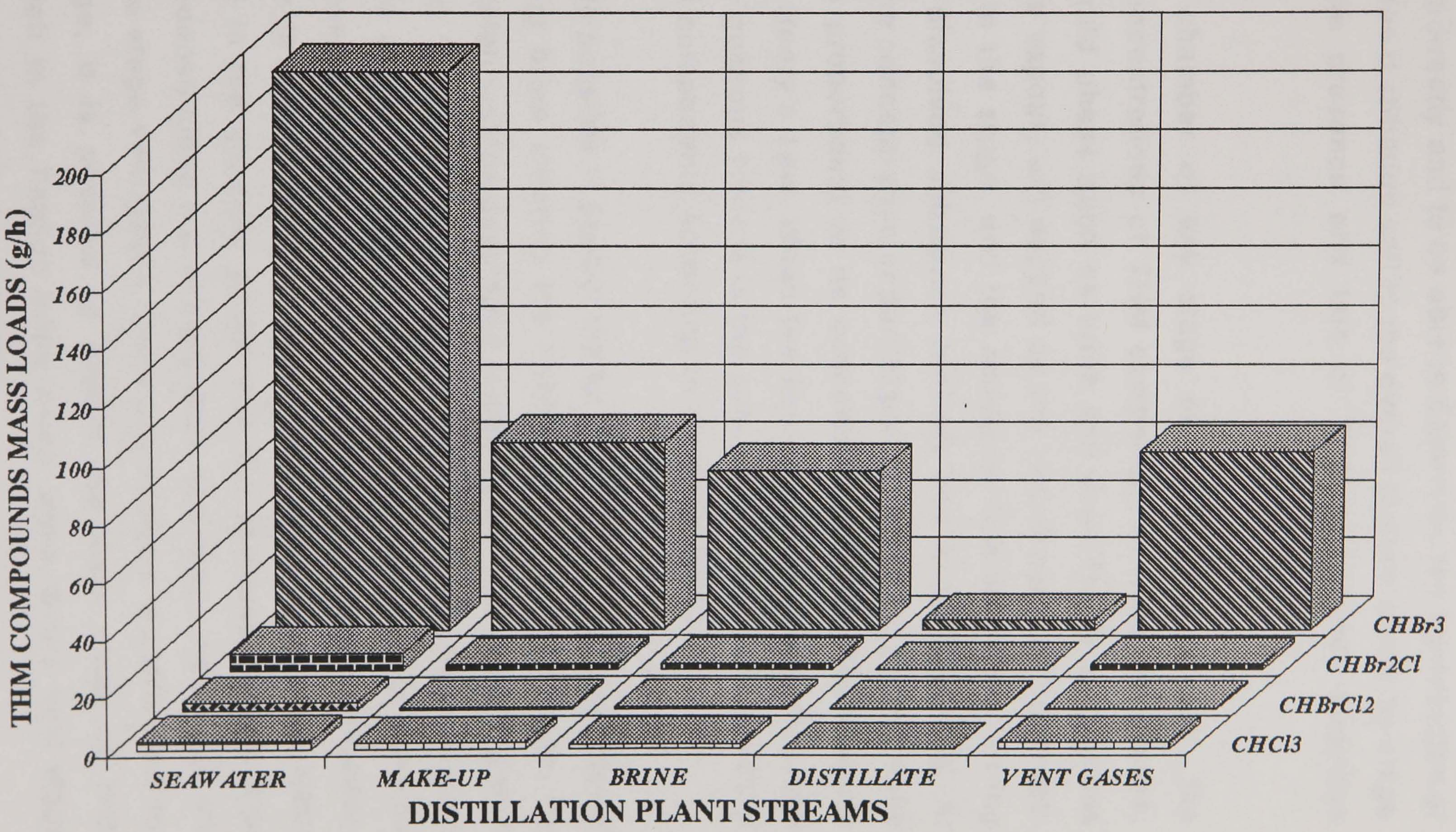


FIGURE 12
THM COMPOUNDS FORMATION POTENTIAL



out appropriate mass balances on the whole unit. In order to confirm these results indirectly and to be able to determine the contribution of each stage of the distillation unit to the overall picture, stage-by-stage analysis of the presence and fate of *THM* compounds becomes necessary.

In the flash chamber of any stage of the distillation unit, the equilibrium concentrations of *THM* compounds in different phases, whether in liquid phase such as brine and distillate or in gaseous phase such as vapour, will depend on the temperature of the stage, the pressure in the stage, and the molecular interactions occurring between the dissolved substance (*solute*) and water (*solvent*). At equilibrium, the concentration or partial pressure of a substance in the gas phase is proportional to its concentration in the liquid phase according to *Henry's Law.* When the liquid phase is ideal, the total pressure of a gaseous mixture is the sum of the partial pressures of the individual components according to *Dalton's Law.*

Therefore, it is possible to predict the fate of *THM* compounds present in the flashing brine entering the flash chamber of any stage. By utilising the relationships developed in **Appendix I**, and starting with the measured *THM* compounds concentrations in the recirculating brine, the fate of these compounds within the distillation unit can be predicted. Based on the conditions existing within any flash chamber, it is possible to calculate how much of the *THM* compounds mass loads will be in the gaseous phase with the released vapour, how much will condense along with the distillate, and finally, how much will leave with the stage vent gases. Once this analysis is carried out for a given stage, it is possible to predict the mass loads of *THM* compounds left in the flashed brine which move to the next stage where the above analysis is repeated.

Every stage within the distillation unit has its unique conditions regarding temperature, pressure, brine salinity and brine flow rate. To be able to carry the above analysis as outlined in **Appendix I**, it is necessary to know the above parameters of each stage. **Figure 13** maps the average temperature and pressure of the distillation unit stages, while **Figure 14** shows the flashing brine flow rate and salinity in every stage, based on summer design conditions.

In addition, the dependence of *Henry's Law* constant (**H**) on temperature must be determined. This dependence is given by the following equation :-

$$Ln\,(\mathbf{H}) = \frac{-a}{T} + b \qquad \text{Eq. 28}$$

The values of constants a & b in the above equation have been estimated by many authors[342]. The estimates, which suffers from relatively large variance, are mostly based on laboratory studies and with certain types of water, usually distilled water. Furthermore, most estimates are related to only one of the four *THM* compounds under consideration; namely, chloroform.

By performing iterative computer analysis, it was possible to predict values for the above mentioned constants, which yielded the most matching results with the actually measured values. **Table 17** lists values obtained from the literature along with predicted values of these constants. By utilising the predicted values of these constants, it was possible to predict the mass loads and concentrations of *THM* compounds on a stage-by-stage basis and on an overall basis.

Based on the above analysis, a prediction of the mass loads and concentrations of *THM* compounds in the distillate product and the

FIGURE 13
STAGE-BY-STAGE FLASHING-CONDENSING

TEMPERATURE & PRESSURE

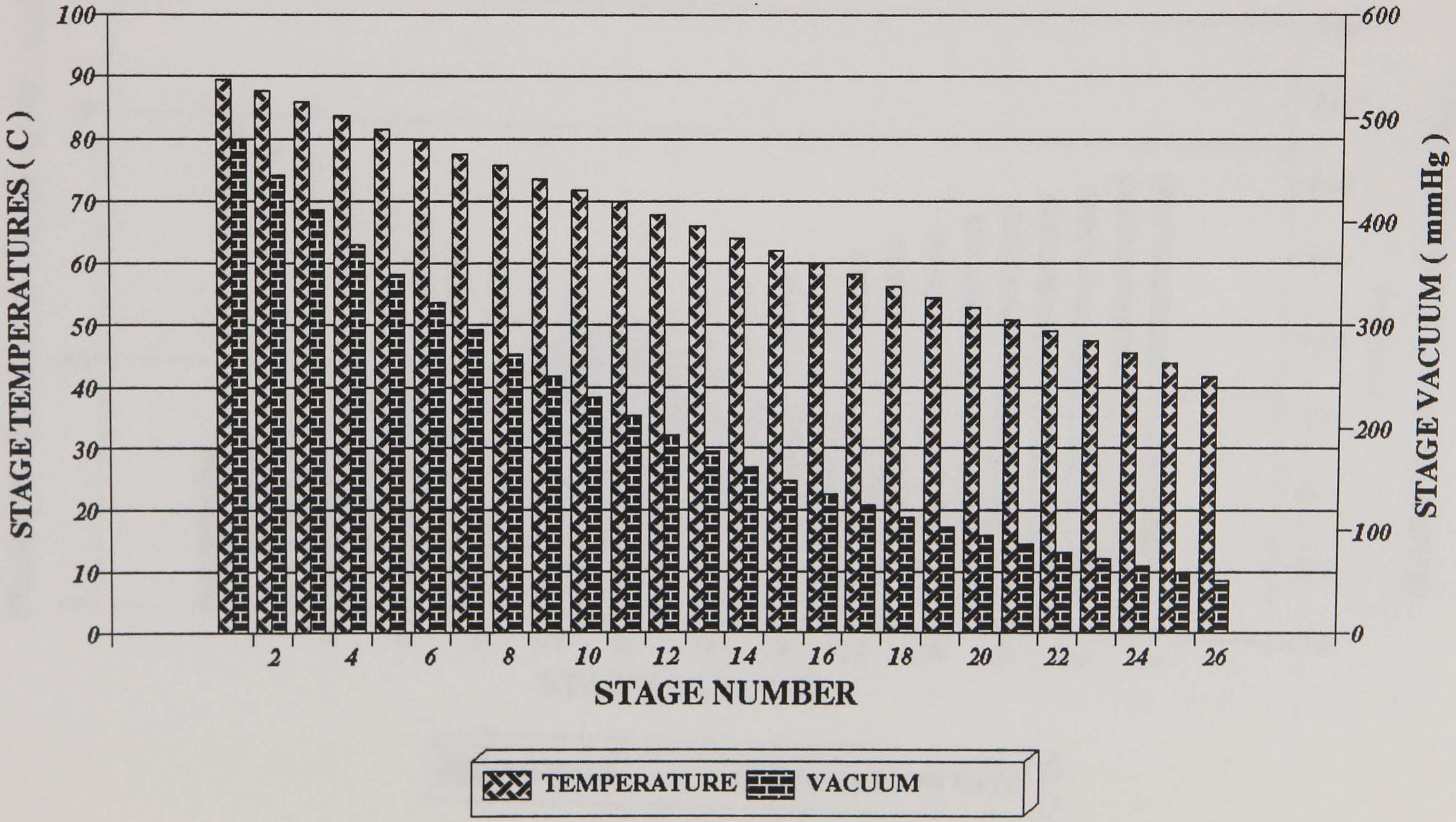


FIGURE 14
STAGE-BY-STAGE FLASHING BRINE STATUS

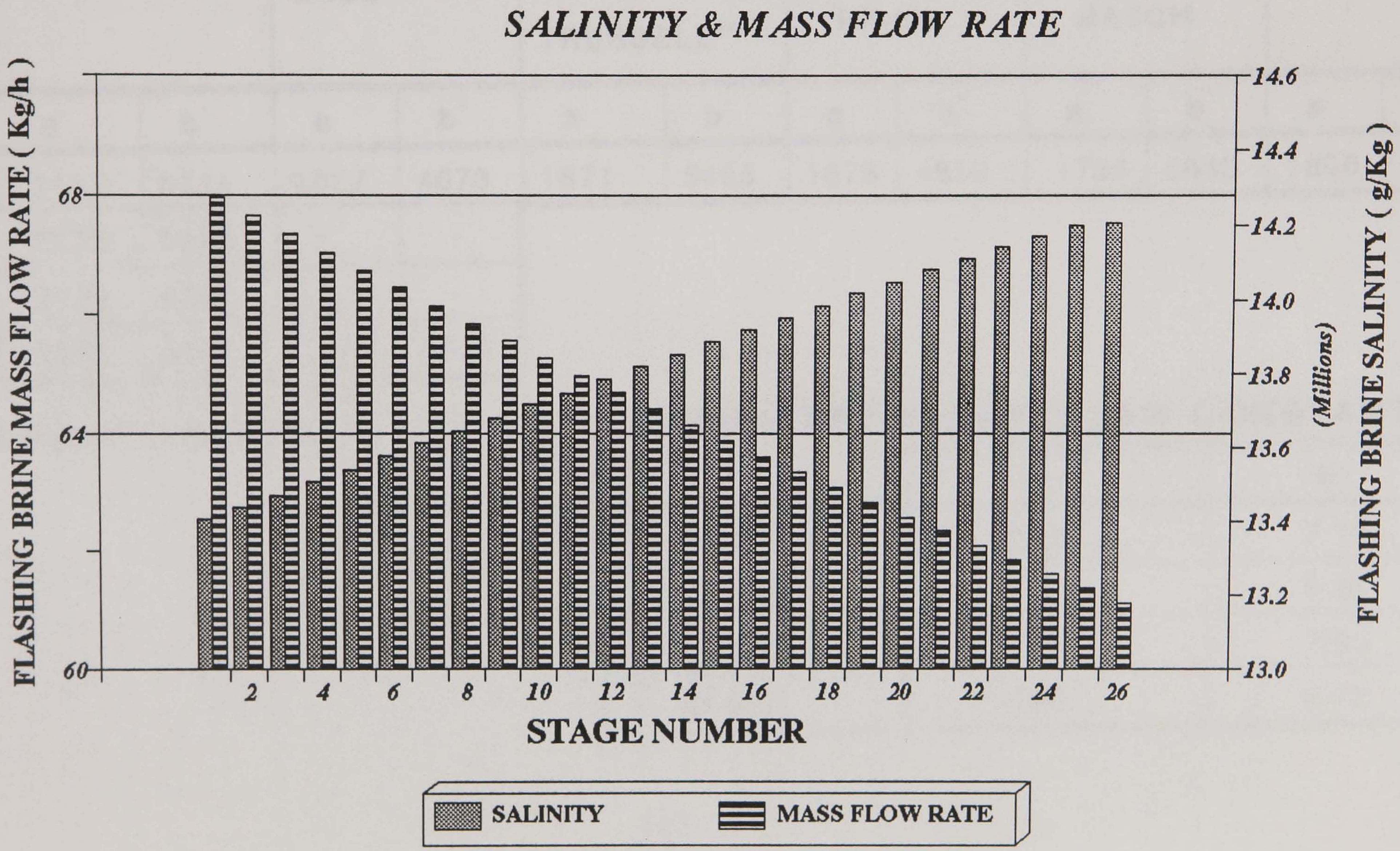


TABLE 17
HENRY'S LAW TEMPERATURE DEPENDENT CONSTANTS VALUES

	NICHOLSON[343]		LEIGHTON & CALO[344]		KAVANAUGH & TRUSSELL[345]		GOSSETT et al.[346]				MUNZ[347]	
							EPICS		BATCH			
	a	b*	a	b*	a	b*	a	b*	a	b*	a	b*
$CHCl_3$	2117	6311	1627	4673	1871	5495	1675	4859	1736	5033	1800	5234
$CHBrCl_2$	2122	5495	-	-								
$CHBr_2Cl$	2122	5790	-	-								
$CHBr_3$	2322	6181	1627	4673								

* - All figures should be multiplied by 10^{-3}

PREDICTED HENRY'S LAW CONSTANTS

	a	b
$CHCl_3$	2000	7.17
$CHCl_2Br$	1800	5.86
$CHClBr_2$	2000	7.65
$CHBr_3$	1950	6.72

vent gases of the distillation unit can be made. **Table 18** compares the measured and predicted values for *THM* compounds concentrations and mass loads. The agreement between the measured and predicted set of values is considered to be very good.

Figure 15 maps *TTHM* compounds mass load in flashing brine, distillate product and vent gases of every stage. The figure also shows the substantial contribution of the vent condensate to the distillate *TTHM* compounds mass load. This is explained by the fact that the vent gases are very concentrated with *THM* compounds when they leave the stages. As they pass through the vent condensers, they tend to partially condense, along with most of the vapour present in the vent gases, in quantities which are governed by the prevailing temperature and pressure. It can be shown that the release of *THM* compounds from the flashing brine of any stage and the condensation of these compounds along with the distillate, is a function of the relevant value of *Henry's Law* constant (H), and, therefore, of the conditions existing inside the stages such as temperature and pressure.

As it was not possible to sample the vent gases of the distillation unit in a fashion which is accurate and representative, it was very useful to determine whether it is possible for the above analysis to predict the concentrations and mass loads of *THM* compounds in the vent gases expelled from the distillation unit. **Table 19** gives the anticipated mass loads of *THM* compounds in the vent gases due to the deareation of the last stage, in the vent gases from the stages, in the condensate from the vent condenser and in the vent gases expelled to the atmosphere. It should be remembered that the comparatively small amount of *THM* compounds in the vent gases that will condense after passing through the vent condensers will be added to the unit distillate product, does consisting a substantial contribution

TABLE 18
COMPARISON BETWEEN MEASURED AND PREDICTED THM COMPOUNDS CONCENTRATIONS AND MASS LOADS IN DISTILLATE

COMPOUND	MEASURED VALUES		PREDICTED VALUES	
	CONCENTRATION (µg/L)	MASS LOAD (g/h)	CONCENTRATION (µg/L)	MASS LOAD (g/h)
$CHCl_3$	0.00	0.00	0.04	0.04
$CHBrCl_2$	0.38	0.43	0.06	0.07
$CHBr_2Cl$	0.00	0.00	0.00	0.01
$CHBr_3$	2.67	3.03	2.64	2.83
TTHM	3.05	3.45	2.75	2.95

FIGURE 15

STAGE-BY-STAGE THM COMPOUNDS ANALYSIS

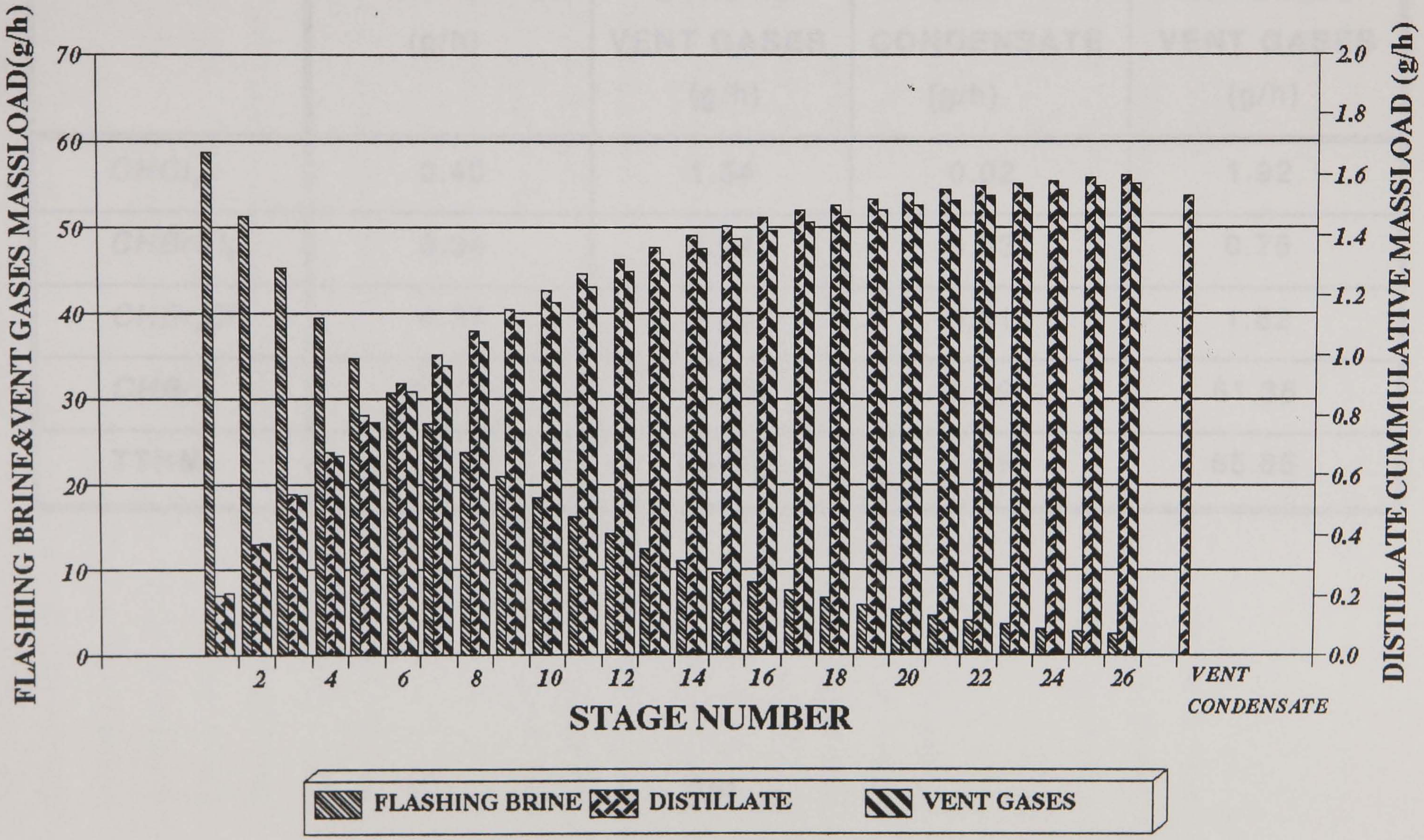


TABLE 19
PREDICTED THM COMPOUNDS MASS LOADS IN VENT GASES

COMPOUND	DEAREATION (g/h)	STAGES VENT GASES (g/h)	VENT CONDENSATE (g/h)	EXPELLED VENT GASES (g/h)
$CHCl_3$	0.40	1.54	0.02	1.92
$CHBrCl_2$	0.34	0.44	0.03	0.75
$CHBr_2Cl$	0.37	1.46	0.01	1.82
$CHBr_3$	11.09	51.56	1.29	61.36
TTHM	12.20	55.00	1.35	65.85

to the *THM* compounds concentration. However, the majority of *THM* compounds in the vent gases will end being discharged to the atmosphere.

4.9 Conclusions

Based on the results obtained from the monitoring programme carried out on two identical distillation units located at **Doha East Power Generation & Water Production Station** in **Kuwait**, the following conclusions could be made:-

1. The extent of formation of *THM* compounds during the chlorination of sea water is a function of both residual chlorine and temperature. *THM* compounds formation increases linearly with increasing residual chlorine and exponentially with increasing temperature. It was very evident that when chlorination dosage increases, the concentration of *THM* compounds and, thus, their corresponding mass loads increases. This is clearly demonstrated during shock chlorination practice. The effect of temperature was also clearly observed. *THM* compounds concentrations and mass loads were substantially higher during the summer season compared to the spring season.

Based on the data obtained from the two units included in the monitoring programme, the overall average total concentration of *THM* compounds in chlorinated sea water was **22.19** µg/L, ranging from maximum of **39.92** µg/L to a minimum of **3.39** µg/L. The corresponding overall average total mass load was **203.08** g/h, ranging from a maximum of **385.89** g/h to a minimum of **33.63** g/h. A clear correlation was evident between *THM* compounds concentrations and mass loads on the one hand and chlorination dosage and water temperature on the other hand. The correlation was much stronger in the case of temperature, whereby maximum concentrations and mass loads occurred during when sea water temperature was at its highest.

2. It can be said that at a given concentration of residual chlorine and sea water temperature, *THM* compounds concentrations and mass loads increase with increasing contact time. It can also be inferred that when available residual chlorine is present, the potential for *THM* compounds increase with increasing *TOC* content.

The impact of contact time could be clearly shown by comparing the concentrations of *THM* compounds in chlorinated cooling sea water feeding the two distillation units. As the two units share the same water and are served by the same intake system, the difference in the concentrations of these compounds must be due to the effect of contact time which is linked to their relative distance from the point of chlorination. Therefore, the contact time in the case of sea water feeding **A6** distillation unit is expected to be slightly higher than that for **A4** distillation unit. As a consequence the average total concentration of *THM* compounds in sea water in the case of **A4** distillation unit was **20.88** ± **5.64** µg/L, while the average total concentration of these compounds in the case of **A6** distillation unit was **23.49** ± **12.21** µg/L. The fact that sea water temperature and *pH* were nearly identical in both cases and that the average residual chlorine were **0.18** mg/L and **0.10** mg/L, respectively, lends weight to the supposition that at least some of the above difference in the concentrations of *THM* compounds is due to the effect of contact time.

3. A substantial amount of *THM* compounds mass loads formed during the chlorination process of sea water is discharged back to the sea, thus, creating a possible adverse environmental impact. Based on a distillation unit of 27276 m^3/day (6.0 MIGPD) an overall average *THM* compounds total mass load of **203.08** g/h is formed as a result of the

chlorination of sea water, whereby **133.96** g/h representing **65.96%** is discharged back to the sea along with the excess cooling sea water. The remaining *THM* compounds total mass load of **69.12** g/h representing **34.04%** enters the distillation unit via the make-up feed. Under continuous chlorination practice, it has been concluded that no *THM* compounds are discharged with the blowdown brine as it has been shown that by the end of the distillation cycle all of the *THM* compounds content in the recirculating brine is removed due to the repeated flashing process.

4. It has been shown that most of the input *THM* compounds mass loads to the distillation unit end up being removed through the vent gases. Thus, it could be concluded that the multi-stage flash distillation process is very efficient in removing these compounds, achieving a percentage removal of just over **95%**. Out of the average *THM* compounds total mass load of **69.12** g/h entering the distillation unit via the make-up feed, **65.67** g/h is removed along with the vent gases, whereby **10.55** g/h (**15.26%** of *THM* input) is removed due to deareation in the last stage and **55.12** g/h (**79.75%** of *THM* input) is removed due to the venting in each stage. The overall average total mass load of *THM* compounds in the distilled water produced was found to be **3.45** g/h, representing **4.99%** of *THM* compounds mass load in the make-up feed and **1.69%** of *THM* compounds in the chlorinated sea water. Out of the above total mass load of *THM* compounds in the distillate, a substantial amount of **1.35** µg/L is due to the addition of vapour condensate from the vent gases which is condensed in the distillation unit vent condensers and returned to the distillate product in the last stage. The exceptional removal capability of the distillation unit must be linked to the dynamic and violent conditions existing inside the flash chambers of the distillation unit which are characterised by boiling and flashing but is also in part linked to the volatility of trihalomethane compounds.

5. A theoretical prediction regarding the fate of *THM* compounds inside the distillation unit and stage-by-stage behaviour can be obtained based on *Henry's Law*. The agreement between the measured and predicted values, based on newly assumed values for constants used to calculate *Henry's Law Constant* (H), is extremely good. It is believed that these newly assumed values, are more accurate compared to those available in the literature, due to the fact that they have been derived under real operational conditions and have been verified by actual experimental data. It is clearly evident that the fate of *THM* compounds within the distillation and their distribution between the different streams within a specific stage is a function of *Henry's Law Constant* (H) which is in turn a function of the conditions existing inside the stage such as temperature and pressure.

6. Anti-scalent and anti-foaming additives will only lead to increased *THM* compounds formation during shock chlorination practice, where high residual chlorine is present which is required for further formation of *THM* compounds, enhanced by the relatively higher temperatures of make-up feed and increased contact time. During shock chlorination practice of **A4** distillation unit, the average total *THM* compounds concentration and mass load were **37.95** ± **6.86** µg/L and **344.04** ± **69.89** g/h, respectively. The corresponding values in the case of make-up feed were **41.63** ± **11.90** µg/L and **121.88** ± **35.17** g/h, respectively. *THM* compounds average total concentration in the distillate was found to be **7.89** ± **5.43** µg/L while the total mass load was estimated to be **9.01** ± **6.31** g/h. *THM* compounds removal due to the distillation process amounted to **112.87** g/h, indicating removal percentage of **92.6%**, of which **12.5%** was due to deareation. Both of the above percentages were slightly lower than those observed during continuous chlorination practice.

7. The most dominant *THM* compound in all streams was found to be bromoform. This is believed to be due to the high level of bromide ions concentration in sea water utilised by the distillation unit. The percentage relative contributions of bromoform to the total *THM* compounds present were **94.4%**, **93.3%** and **87.5%** in the case of chlorinated sea water, make-up feed and distilled water, respectively. In addition, distilled water was also characterized by relatively high presence (**12.5%**) of bromodichloromethane.