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TRIHALOMETHANES (THMs) FORMATION IN A DISTILLATION PROCESS

BASSAM TAWABINI[1], HRAJ KHARARJIAN[2] and NABIL FAYAD[3]

[1,3]Research Institute, P.O.Box *952,* Dhahran 31261, Saudi Arabia

[2]Civil Engineering Department, King Fahd University of Petroleum & Minerals,
KFUPM Box 1754, Dhahran 31261, Saudi Arabia

ABSTRACT

In this study, the fate of THMs -formation .in seawater distillation process and the rates of THMs formation in the chlorinated blended distillate were examined under various experimental conditions. The following general equation was obtained empirically:

$$\text{Log (THM)} = A * \text{Log} (Cl_2) + B * \text{Log (TOC)} + C$$

(THM) is the concentration of total THMs in μg/l, (Cl_2) and (TOC) are the concentration of chlorine doese and total organic carbon in mg/l, A,B, and C are estimated parameters. The results showed that THMs level increases with the increase of both chlorine and initial humic substances concentrations. Increase in temperature and contact time also increased THMs concentrations. On the other hand, pre-chlorination and aeration step of the seawater resulted in a reduction of THMs concentrations in the blended distillate.

INTRODUCTION

In 1974, Rook (1) and Bellar (2), studied the incidence and possible formation of low molecular weight halogenated hydrocarbons in municipal drinking owater, and found that chlorinated hydrocarbons form as a result of the chlorination process during water treatment. In the same year, the National Organic Reconnaissance Survey (NORS) of the United States (3) showed that halogenated organic compounds were found in every U.S. drinking water tested. Trihalomethanes (THMs) such as: chloroform, bromodichloromethane, dibromochloromethane, and bromoform, were the main substances among the halogenated organics found in that survey. In recent years, increased attention has been given to THMs formation in drinking water as a result of the evidence that some of the THMs have carcinogenic properties (4). For this reason, the U.S. Environmental Protection Agency (EPA, 1979) proposed a maximum contaminant level (MCL) of 100 μg/l for total THMs in finished drinking water (5). THMs in general are present at very low concentration in the raw (i.e. unchlorinated) water sources. They are formed in the water during the process or disinfection when chlorine reacts with humic substances normally present in water.

The major source or domestic water supply in Saudi Arabia is seawater from which desalinated water is prepared. Drinking water distributed to the inhabitants is a blend or raw well water and desalinated water. Desalination or the seawater by the Multi-Stage Flash Distillation represents the most

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widely technique used for obtaining desalinated water from the sea in Saudi Arabia. Chlorination is the widely applied disinfection method to water before the water is pumped into the distribution system. Field studies (6) have shown that THMs were detected in several locations of the water distribution system of the Eastern Province of Saudi Arabia. However, review of literature revealed no studies related to the THMs formation in a distillation process. Therefore, it became necessary to conduct such studies in order to evaluate the effect of various parameters on the THMs formation in distillation processes. This paper discusses the effects of variation of humic substances concentration and chlorine dose on the THMs formed in the seawater and blend of the distilled product water and ground water, and the development of empirical relationship describing the formation of THMs under various condition. Also, the effect of contact time, temperature and aeration on THMs levels in the blended distillate water was investigated.

MATERIALS AND METHODS

All experiments were carried out using a synthetic seawater which was prepared in the laboratory by dissolving various chemicals in distilled water as shown in Table (1).

TABLE 1

The amounts of the chemical compounds added to distilled water to make synthetic seawater

Chemical Compounds	Concentration (mg/l)
Na_2SO_4	6.02
$NaHCO_3$	0.168
NaCl	24.0
$MgCl_2.6H_2O$	17.73
KCl	7.46
$CaCl_2.2H_2O$	2.75
KBr	0.075

Stock solution of the humic substances (HS) was extracted from Gulf seawater according to the procedure described by Mantoura & Riley (7) using XAD-2 resin. Desorption of the HS extract was carried out by 1.0 M methanol-ammonia solution. The eluant was collected and evaporated and the yellowish residue was dissolved in 60 ml of distilled water. The Total Organic Carbon (TOC) of this stock was found to be 150 mg/l. This solution was used to prepare synthetic seawater which contains various concentrations of the humic materials. Chlorination of the water samples was carried out using sodium hypochlorite solution (NaOCl) and the final concentration of the residual chlorine was measured using the DPD standard method (8). During the experiment, chlorine was added into two stage. In the first stage, chlorine was added to the seawater before distillation process referred to as "prechlorination". In the second stage, chlorine was added to the distillate blended with groundwater referred to as "post chlorination".

EXPERIMENTAL PROGRAM

The experimental work was carried out mainly into four parts as shown in Fig. (1).

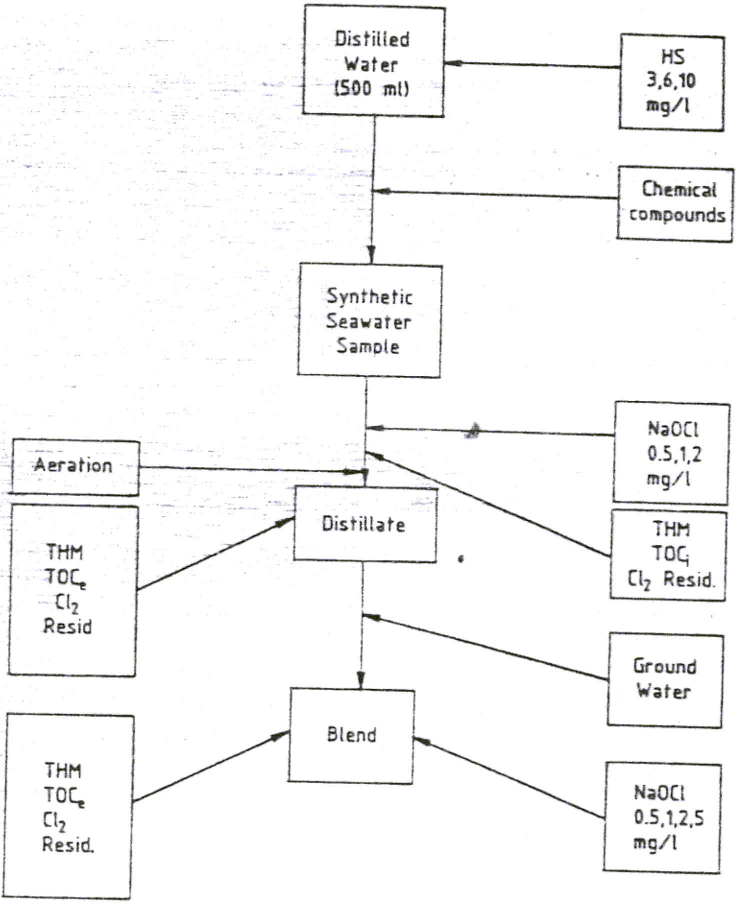

Fig. 1. Experimental Work Layout.

In the first part, the synthetic seawater samples dosed with humic substances at concentration of 3, 6 and 10 mg/l were chlorinated at chlorine concentration of 0.5, 1.0 and 2.0 mg/l. THMs formed in these samples, after 24 hours, were analyzed. In the second part, unchlorinated synthetic seawater samples were distilled and blended with raw ground water at a ratio of 7:1 to obtain a blend of TDS of 400-500 mg/l. The blend was then chlorinated with NaOCl at concentration of 0.5, 1.0, 2.0 and 5.0 mg/l. THMs formed in these samples were analyzed. In the third part, the seawater samples were prechlorinated at concentrations of 0.5, 1.0 and 2.0 mg/l prior to distillation. The distillate blended with raw water was then postchlorinated at concentrations of 0.5, 1.0, 2.0 and 5.0 mg/l and then analyzed for THMs. Finally, part three was repeated with introduction of an aeration step before distillation. THMs were analyzed before and after aeration.

ANALYTICAL METHOD

Liquid-Liquid Extraction (LLE) (9) method was used for the extraction of THMs from the water samples using pentane as a solvent. The analysis of THMs compounds was carried out using a Varian Model 3700 gas chromatograph which is equipped with Ni63 Electron Capture Detector and 3390A Model HP integrator. A 30 m long fused silica capillary column, 0.25 mm I.D., coated with a thick film of the stationary phase (1 µm) DP-5 was used for chromatographic separation of the THMs components. The GC even temperature was programmed from 50°C to 100°C at a ramp rate of 5°C/min with an initial hold time of 4 minutes. Nitrogen gas was used as the carrier gas with a flow rate of 2 ml/min, detector base flow at 12 ml/min and carrier makeup gas at 16 ml/min. The detector and injection port temperatures were 330 and 270°C respectively.

RESULTS AND DISCUSSION

A typical chromatogram showing the THMs formed in a seawater sample at initial TOC of 3.0 mg/l and chlorine dosage of 1.0 mg/l is shown in Figure (2).

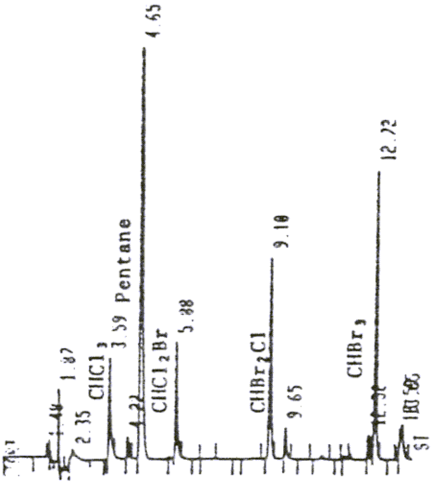

Fig. 2. A chromatogram showing the THMs formed in a synthetic sea water sample at TOC_i of 3.0 mg/l and Cl_2 of 1.0 mg/l

The changes of the total THMs concentration in chlorinated seawater dosed with humic substances concentration of 3, 6, and 10 mg/l measured as TOC are shown in Figure (3).

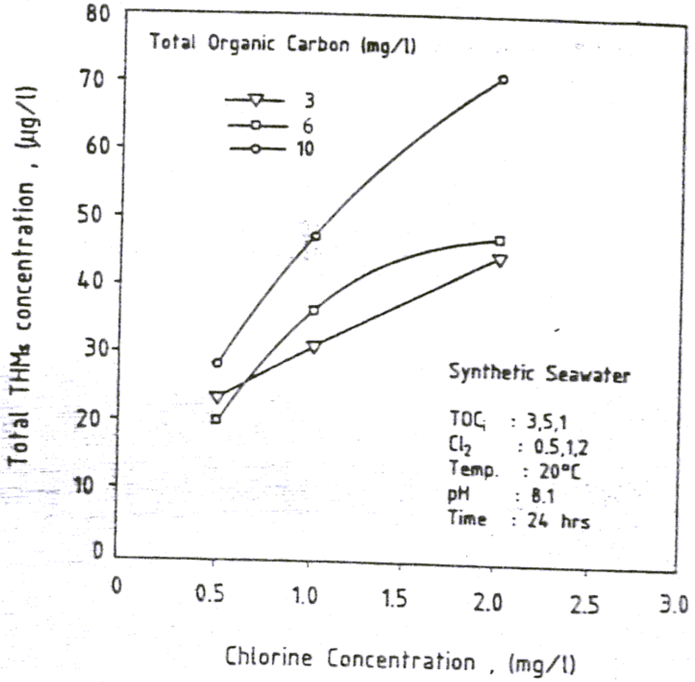

Fig. 3. Total THMs concentrations in chlorinated seawater at various TOC concentrations

It can be seen from Figure (3) that for a given TOC concentration the THMs level increased as chlorine dosage increases from 0.5 to 2.0 mg/l. The incremental increase is approximately linear at TOC of 3 mg/l and not linear at other TOC concentrations. THMs concentration also increased as TOC increased from 3 to 10 mg/l.

Trihalomethanes were not detected in samples of raw water blended with distillate and collected immediately after the distillation process. THMs were not detected for these samples even with high doses of chlorine in the seawater. However when chlorine was added to the blended sample, THMs started forming. The changes of the total THMs concentration formed in the blended distillate is shown in Figure (4). Again, the total THMs levels were increasing as both chlorine dose and TOC increased.

The variations of the total THMs levels in the blended distillate samples after pre chlorination of 0.5, 1.0 and 2.0 mg/l are shown in Figures (5), (6) and (7) respectively. The same phenomena of increase in THMs formation with increasing chlorine dose was observed. The THMs decreased as TOC increased from 3 to 6 mg/l but it increased again when TOC was 10 mg/l. It is also

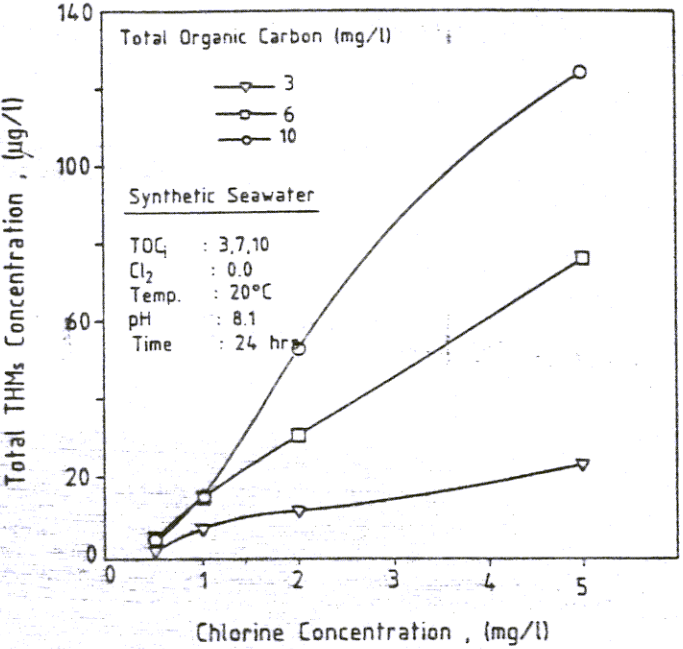

Fig. 4. Total THMs formed in distilled seawater at various chlorine and TOC concentrations

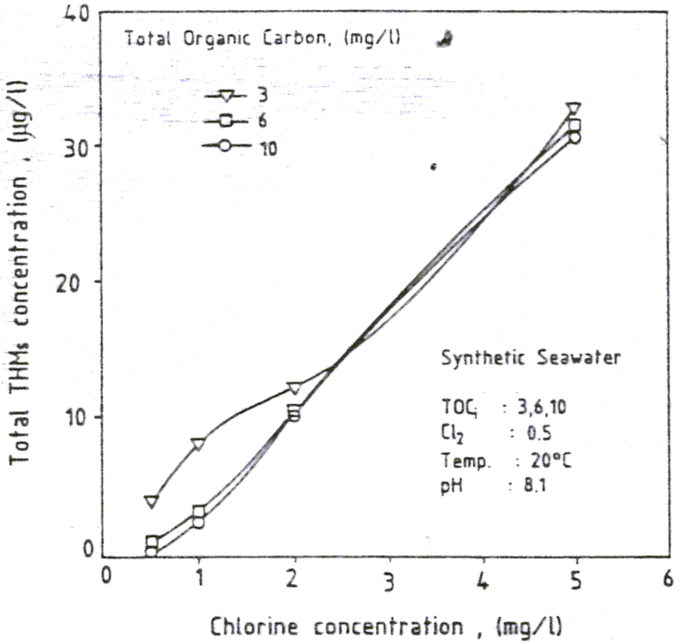

Fig. 5. Variation of total THMs concentration levels with chlorine for distilled synthetic sea water

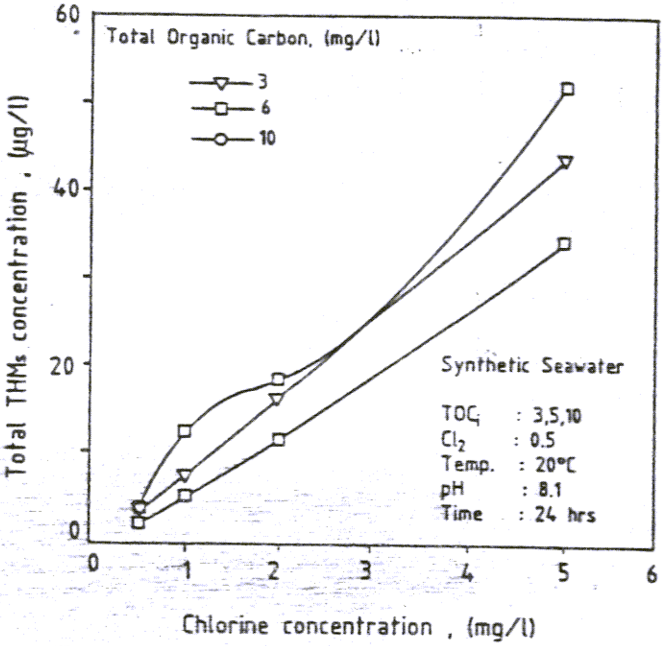

Fig. 6. Variation of total THMs concentration levels with chlorine for distilled synthetic sea water

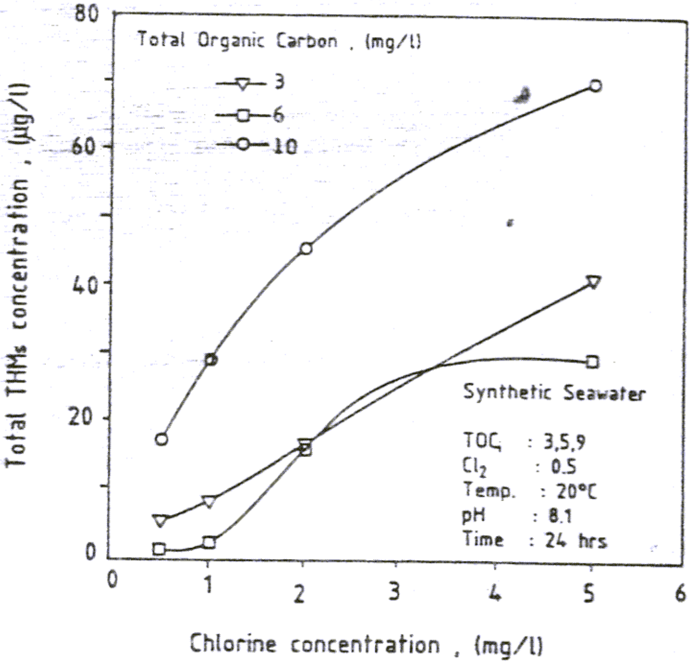

Fig. 7. Variation of total THMs concentration levels with chlorine for distilled synthetic sea water

observed that the THMs concentrations formed when seawater was distilled after prechlorinated were about 30% lower than without prechlorination.

A typical bar chart which shows the level of the various THMs components in the total THMs is shown in Figure (8).

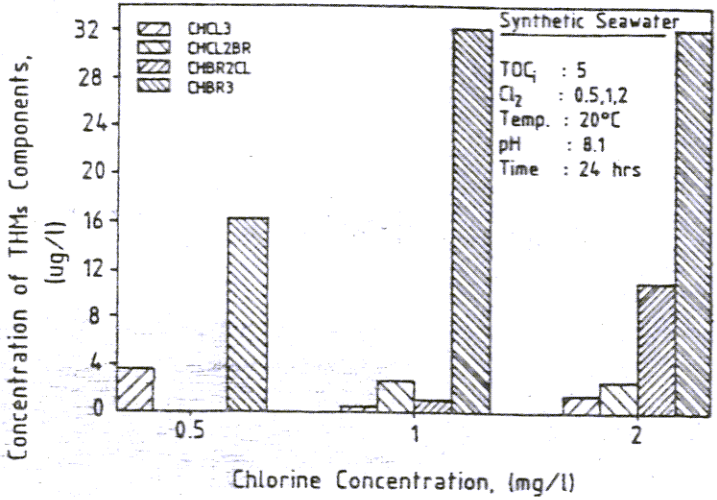

Fig. 8. THMs concentration levels in chlorinated sea water at 5.0 mg/1 TOC concentration

It can be seen that bromoform was the major THMs formed in the chlorinated sea water. This was attributed to the presence of high concentrations of bromide ion in the seawater. Other investigators (10), have achieved similar result and have shown that bromide ions are oxidized by aqueous chlorine to intermediates which apparently participate in the THMs formation much more effectively than does chlorine.

The effect of aeration on the concentration level of THMs was also investigated. The results showed that around 50% reduction in THMs concentration in the seawater was obtained when the chlorinated seawater was purged with helium gas for 15 minutes at a flow rate of 7 liter/min. as shown in Table (2).

TABLE 2

THMs concentrations formed in the synthetic sea water at chlorine concentration of 2.0 mg/1 before and after aeration

Distil-lation	Aerati-on	time hour	RES-C12 mg/L	temp deg	TOCe mg/L	CHCL3 µg/L	CHCL2BR µg/L	CHCLBR2 µg/L	CHBR3 ug/L	TTHMs µg/L
before	before	24	1.17	18	10.0	ND	6.1	17.8	141.7	165.6
before	after	24	0.67	20	8.0	ND	3.3	10.0	69.1	82.4
% difference			42.7		20	0.0	45.9	43.8	51.2	50.2

The best fitted relationship was found to be logarithmic as shown in Fig. (9). In general, the best fit model found was as follows:

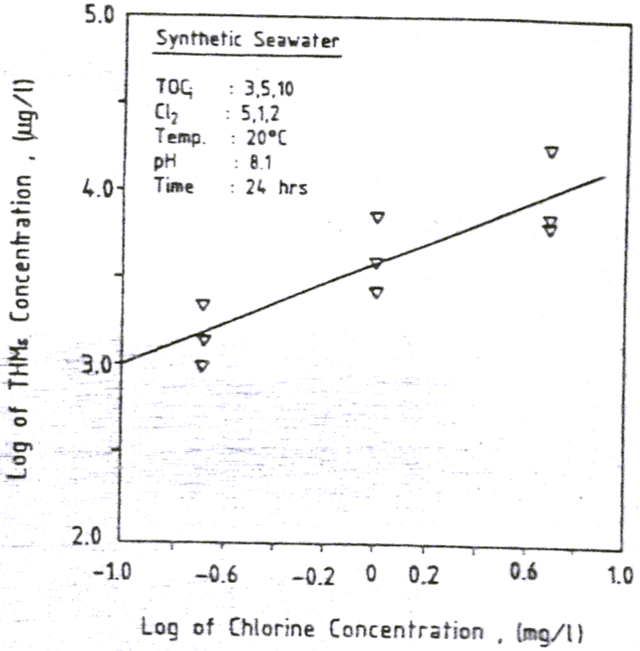

Fig. 9. Logarithmic plots of total THMs concentration in chlorinated synthetication water at various TOC concentration vs. chlorine concentration

The effect of contact time and temperature on THMs formation in blended distillate samples were analyzed for THMs at different times and temperatures, as shown in Figures (10) and (11). It was found that THMs concentration levels is directly proportional to contact time and temperature according to the following formulas:

$THMs = 10.98 + 0.28t$ $\quad R^2 = 0.9948$

for $t > 1$ hr

$THM = THM_{20} * 1.025^{(T-20)}$ $\quad R^2 = 0.9936$

for $T > 21°C$

THM_{20} = THM level at 20°C

$$\text{Log [THMs]} = A + B \text{ Log } [Cl_2] + C \text{ Log [TOC]}$$

where [THMs] is the concentration fo the total trihalomethanes formed in μg/l, Cl_2 is the chlorine dosage in mg/l; and [TOC] is the initial concentration of HS in mg/l in the seawater. A, B and C are the estimated parameters. A list of the estimated parameters (A,B,C) and the correlation coefficient (R^2) for the blended distillate under the given conditions are listed in Table 3.

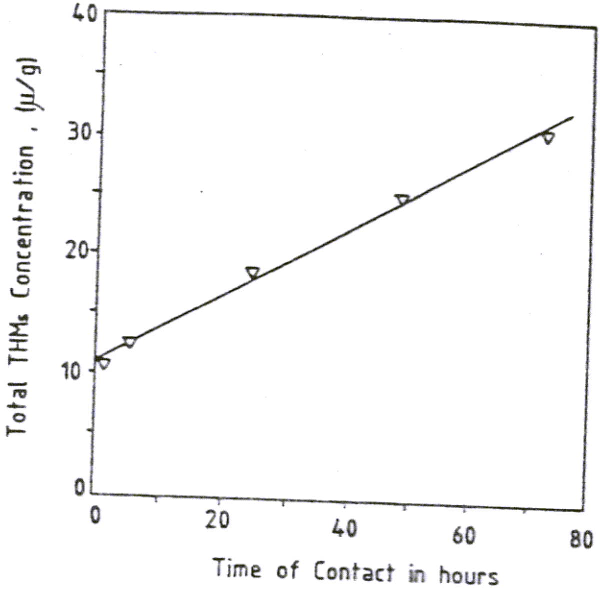

Fig. 10. THMs concentrations formed in the distilled seawater at different contact times

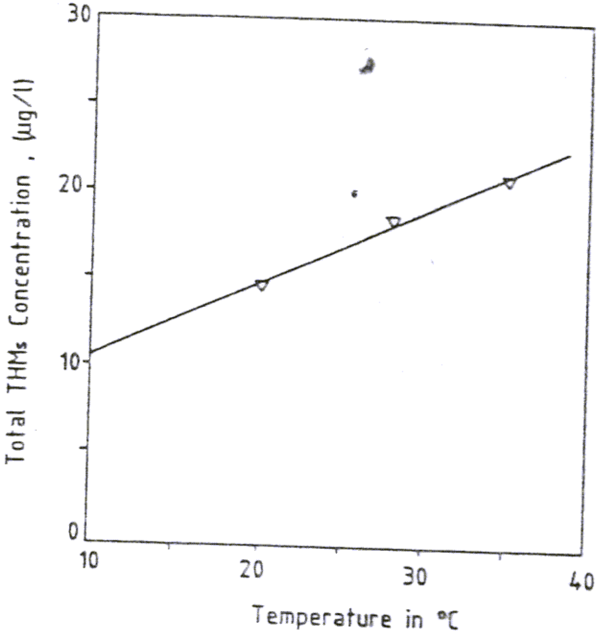

Fig. 11. THMs concentration formed in the distilled seawater at different storage temperatures

The coefficients A,B,C for the seawater chlorination were 3.091, 0.58 and 0.287 respectively.

TABLE 3

The estimated parameters (A,B,C) of the models representing the experimental data under various conditions

Total Organic Carbon in Seawater (mg/l)	Seawater Chlorine Dose (mg/l)	A	B	C	D
3, 7, 10	0.0	-0.05	1.425821	1.184261	0.9277
3, 6, 10	0.5	2.406	1.344220	-0.60929	0.9115
3, 5, 10	1.0	2.488	1.194127	-0.36221	0.9529

CONCLUSIONS

In the light of the results obtained in this study, the following conclusions can be drawn:

1. The experimental results have shown that THMs were formed in the chlorinated synthetic seawater samples, which contained humic substances and also in the chlorinated blended distillate samples.
2. The major THM component in most of the experiments were the bromoform ($ChBr_3$), measuring more than 50% of the total THMs.
3. The formation of THMs was directly proportional to the concentration of the chlorine for a given level of HS concentration.
4. THMs formed in the distillate of unchlorinated seawater increased as initial HS level increased, however, this relation was reversed when the seawater was prechlorinated with 0.5 and 1.0 mg/l of sodium hypochlorite. Moreover, when the seawater was prechlorinated with 2.0 mg/l, THMs in the distillate were again increasing with increasing seawater HS levels.
5. The THMs formed in the distillate of chlorinated synthetic seawater were in general lower than those formed in the distillate of unchlorinated synthetic seawater.
6. No THMs were detected in the water samples collected immediately after distillation process. The chlorine and TOC were also not detected in such samples. This means that the distillation process is very effective in removing THMs, TOC and chlorine. However, reformation of THMs was observed when chlorine was added to the distillate samples.
7. The results of this study show that stripping the seawater samples with an inert gas is effective in reducing THM concentrations by 50%.

8. The formation of THMs was found to be linearly dependent on the contact time.

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