

**6. Study on Countermeasures against Oil Contamination  
of Product Water in MSF Process (MSF-2)**



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## **6.1 Investigation and Preparative Experiment**



## **6.1.1 Introduction**





**1. Introduction**

A survey for quality of seawater in the Arabian Gulf was initially planned to identify levels of oil contents, hence contamination of feed to MSF desalination plants. Since the levels of oil contaminants were negligible, it was not feasible to correlate oil carry over into product water in actual operating plants at such low levels. Therefore confirmation of the accuracy of the computer simulation program was limited to the MSF test plant data where oil was injected into the brine stream.



**6.1.2 Preparative Experiment**  
**(Vaporization Mechanism of Organic Contaminants)**



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## 1. Introduction

In recent years, marine pollution has been one of the major environmental concerns throughout the world. These concerns are not only about ecological problems but also about the possible crises in the daily life of ordinary people, especially in gulf countries where there is only a limited amount of natural drinking water. In these countries, the greater part of the drinking water is produced by seawater desalination plants and massive oil spillage in the vicinity of these plants during the Gulf War struck terror into the hearts of residents (1). Similar pollution might also occur due to some sudden accident of coastal oil wells, oil refineries or tankers. Furthermore, we must also take into consideration a different kind of marine pollution, that has been gradually increasing, caused mainly by various human activities, including industry, farm production and normal everyday living (2).

Till now, most seawater desalination plants have been designed without giving much consideration to these oil spills or the steady increase of marine pollution by the population at large. The only available method of protection recognized at present as preventing these pollutants from entering the seawater intakes of the plants are various type of walls or fences, even though complete removal by this method may be impossible, especially for suspended or soluble pollutants.

MSF(multi-stage flash process) is the most widely used desalination process and approximately three million tons of the water being produced a day in Saudi Arabia at present is with MSF desalination plants(3). When the plant is operated with polluted seawater, there are mainly two concerns, i.e. (1) these pollutants may decrease the performance of the desalination process due to adhesion to the inside of the equipment, and/or (2) the pollutants may transfer to the product water and affect its quality. Since the second concern is related to the health of the people who use the water produced by the plants, we must be especially concerned with this problem.

As regarding the concerns described above, SWCC(Saline Water Conversion Corporation, Saudi-Arabia) and JICA(Japan International Cooperation Agency) have started a collaborative research, named MSF-2. The purposes of this research are as follows;

- (1) to establish the calculation methods that are to be used to anticipate the possibility of contamination by these pollutants in the product water,

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- (2) to propose countermeasures against the contamination of the product water.

This project consists of four parts, described below.

- (1) **Oil Carryover Test** This will be carried out with a laboratory scale evaporator, named Oil Carryover Test Unit on artificial brine that is mixed with various organic substances or oily components. In this section, we establish basic formulas that clarify the vaporization mechanism of the pollutants.
- (2) **Gas-Liquid equilibrium Test** In this test, we will obtain different constants for several hydrocarbons, i.e. Henry's constants, vapor pressures and Antoine's constants. These are required in the simulation study.
- (3) **Computer Simulation Study** Based on the formula and data obtained in the previous parts, calculation methods are established. By these methods, the relative possibility of the contamination of the product water at MSF desalination plants can be calculated.
- (4) **Test Plant Experiment** In this part, we demonstrate the utility of the anticipation method established in part (3) by using the MSF test plant and also study certain correction methods if necessary.

The Oil Carryover Test is the first step of this research and we, therefore, consider the result of this test as establishing the basis of this project.

In 1991, Hamao et al. carried out a preliminary experiment in a SWCC-JICA collaborative research (4). In their study, some qualitative behaviors of fuel oil A were clarified in a laboratory scale evaporator that simulated some MSF conditions, when it contaminated the brine. The Oil carryover test is considered the next step where quantitative behavior of these pollutants can be studied.

## 2. Background

There are some reports that are concerned with quantitative vaporization mechanisms of some pollutants which contaminate water. After due consideration we feel that it would be better to refer to the results of these studies in order to increase the effectiveness of our work.

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One useful study was carried out by Hakuta et. al. (5). In that study, he conducted evaporation experiments on hydrocarbon-water mixed conditions, by using a laboratory scale evaporator wherein they defined the relationship between the amount of vaporized hydrocarbons and that of vaporized water. In this study, some volatile hydrocarbons such as n-octane, benzene and cyclohexane were used and it was found that the equation for steam distillation was applicable to those cases where hydrocarbons did not dissolve in water. The equation is presented below.

$$\frac{W_o}{W_w} = \frac{M_o \cdot P_o}{M_w \cdot P_w}$$

Where

$W_o$  : Weight of the vaporized oil

$W_w$  : Weight of the vaporized water

$M_o$  : Molecular weight of the oil

$M_w$  : Molecular weight of water(18)

$P_o$  : Vapor pressure of the oil

$P_w$  : Vapor pressure of water

In this equation, M and P are the constants, so  $W_o$  is in proportion to  $W_w$ . Therefore, if  $W_w$  is known  $W_o$  can easily be obtained. Vapor pressures of chemicals (including hydrocarbons and water) at various temperatures are obtained from Antoine's equation, described below(6).

$$\log_{10} P(\text{mmHg}) = A + \frac{B}{C + t(^{\circ}\text{C})} \quad (\text{A,B,C, are the constants})$$

In that study, it was demonstrated that the equation was suitable only in the case of an insoluble hydrocarbon as a single contaminant.

Concerning the calculation methods for soluble hydrocarbons, there is a study reported by Hamada(7). In his report, when the vaporization of inert gases follows Henry's law, the concentration of these in the condensate solution in a continuous flow evaporator is obtained according to the following equation:

$$C_c = \frac{m}{R \cdot m + 1 - R} C_s$$

(6.1.2)

$$m = \frac{C_c}{C_r} = \frac{55.5}{H \cdot P_{H_2O}}$$

Where

$C_c$ : Concentration of the gases in the condensate (mol/l)

$C_s$ : Concentration of the gases in the supplied brine (mol/l)

$R = \frac{\text{Produced rate of the condensate}}{\text{Supplied rate of the brine}}$

$H$ : Henry's constant

$P_{H_2O}$ : Vapor pressure of  $H_2O$

$C_r$ : Concentration of the gases in the remaining brine (mol/l)

Vaporization of soluble hydrocarbons is known to follow Henry's law, the above equation is also considered applicable in such cases. However, it is known that this equation is difficult to demonstrate in an experimental batch evaporator because this study supposes continuous flow systems

Of course, there is the possibility that vaporization of soluble hydrocarbons also follows the equation for steam distillation. In this case, the vapor pressure of a contaminant is calculated by using Henry's law.

With regard to countermeasures against oil spillage of MSF desalination plants, a comprehensive investigation was conducted by Japan Industrial Policy Research Institute (2). In this study, some computer simulation methods for anticipating the possibility of the contamination of oil components or trihalomethane in the MSF product water were developed. However, further studies are required for practical demonstrations of this methods.

### 3. Purpose

As described above, the equation for steam distillation is considered the most suitable formula applicable to quantitative studies on the vaporization mechanism of contaminants. If this equation is used, we can easily calculate the amount of vaporized contaminant by comparison with the amount of product water in MSF plants. However, in order to apply the equation to this study, it is necessary to elucidate the issues described below.

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- (1) Is it applicable in the case of a heavy oil component that may remain for more than several days after oil spillage?
- (2) Is it applicable in the case of soluble contaminants such as trihalomethane and BTXs?
- (3) Is it applicable in the case of complex contaminants such as fuel oil A? Are some modifications required to apply this equation in this case?

This time, we carried out 'Oil Carryover Test' in order to clarify these issues and various modification methods of the equation were developed as described below. Further, we held discussions in the course of our research, depending on the results of the study.

### 4. Materials and Methods

#### 4.1 Materials

n-Octane and n-octadecane are used as model insoluble pollutants. Bromoform and toluene are used as model soluble pollutants. In order to study the behavior of complex pollutants, fuel oil A was used. The artificial brine was made by adding 41g of NaCl and 33g of Instant Ocean (Aquarium Systems Inc., U.S.A.) to 1L of water. n-Hexane was used to extract bromoform from the brine in the bromoform-fuel oil A mixture carryover test and carbon tetrachloride was used to extract the other pollutants. All the chemicals used in this study were the highest grades available for purchase.

Fig. 1 shows the experimental evaporator used in this study. This was composed of a rotary evaporator including a condenser, a water bath, an impinger, a vacuum pump, a manometer, a controlled water circulator and tubing (Shibata Scientific Instruments, Japan).

For the quantification of bromoform in the brine, gas chromatography (GC; Model 5880A, Hewlett Packard, U.S.A.) was used, which was connected to a purge trap-auto-injector (PT; Model LSC-2, Tekmar, U.S.A.) and an electrochemical detector (ECD). A GC-mass spectrometry detector (MSD; Model 5970A, Hewlett Packard, U.S.A.) was used to analyze and quantify the other contaminants.

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## 4.2 Experimental Methods

### 4.2.1 Methods for the 'Oil Carryover Test'

The basic procedure for the 'Oil Carryover Test' is described in Appendix 1. Some modifications of the procedures for each of the contaminants were conducted as follows:

In the material balance experiment, all the samples obtained as following the procedure were quantified with the GC.

In the experiments done to obtain the vaporization rates, only the remaining contaminants were quantified. The amount of vaporized contaminants was obtained by subtracting the weight of the remaining from the weight of the initial contaminants.

The initial weights were determined by weighing, in the cases of n-octadecane and fuel oil A and by using the GC, in the cases of bromoform and toluene. The initial weight of n-octadecane in fuel oil A was calculated as a percentage of fuel oil A, i.e. 1.6%.

The bromoform solutions were diluted to appropriate concentrations with HPLC water, before injection into the PT-GC. In the bromoform-fuel oil A mixture carryover test, bromoform was extracted with n-hexane and injected into the GC directly.

The concentration of toluene in the brine was determined with the GC-MSD after extraction with n-hexane.

The general evaporation conditions applied in this study were as follows: The preheating time was 10 minutes. The evaporation conditions were 90 °C and 420mmHg. The evaporation times were from 0 to 60 min.

### 4.2.2 Quantification Methods

The analytical conditions for the GC-MSD were described below:

Column	: Hewlett Packard, HP-1, 25 meters
Carrier gas	: Helium, 10psi
Injection	: 3 $\mu$ l, Splitless

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<b>Injection temperature</b>	<b>: 250°C</b>
<b>Oven temperature</b>	<b>: Initial 50°C, 3min.</b>
	<b>: Rate 10°C/min.</b>
	<b>Final 280°C</b>
<b>Interface temperature</b>	<b>: 280°C</b>
<b>Solvent delay</b>	<b>: 5min.</b>
<b>Scanning Mass</b>	<b>: 50-550 amu.</b>
<b>Mode</b>	<b>: SCAN</b>

The analytical conditions for the GC-ECD were as follows:

<b>Column</b>	<b>: Supelco, Vocal, Fused Silica, 30meters</b>
<b>Carrier gas</b>	<b>: Helium, 10psi</b>
<b>Makeup gas</b>	<b>: Nitrogen</b>
<b>Injection</b>	<b>: 1 µl for direct injections, 5ml for purge trap injections Split ratio 1/60</b>
<b>Injection temperature</b>	<b>: 200°C</b>
<b>Oven temperature</b>	<b>: Initial 35°C, 6min.</b>
	<b>Rate 4°C/min.</b>
<b>Detector temperature</b>	<b>: 250°C</b>

### 4.3 Data Analysis Methods

The data analysis methods are presented in Appendix 2. In these methods, an attempt has been made to apply the equation for steam distillation not only to the vaporization of the insoluble contaminant but also to that of the soluble contaminants.

## 5. Results

### 5.1 Material Balance Experiment

In order to comprehend any experimental errors in the evaporation procedures, a material balance experiment was first carried out. After the procedure, the amount of contaminants which had transferred to the impinger, to the condenser which remained in the brine were quantified by the methods described in 'Appendix 1' and the total amount was compared with the initial amount.

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Table shows the result of this experiment. In these experiments, total recoveries were between 90 to 112% of the initial and therefore it was ascertained that there were not considerable losses of vaporized materials during the evaporation process. Consequently, it was found that the amount of vaporized contaminants could be ascertained by measuring the remaining amount in the brine and subtracting that from the initial amount.

### 5.2 n-Octadecane Carryover Test

This was conducted in order to clarify the equation to be applied to heavy oil components barely dissolved in water. n-Octadecane is one of the major components in fuel oil A. In general, fuel oil A contains one or two percent n-octadecane. These components have been observed to remain for several days after an oil spillage.

As shown in Fig. 2, which represents the solubilities of normal paraffins, the solubility of n-octadecane in water is approximately 10ppb (8,9). Solubility in the brine is considered to be lower than that in water. Therefore, in our experimental conditions, almost all n-octadecane was insoluble and stood independently of the brine (i.e. heterogeneous system).

The tests were carried out as presented in Table 2 and from these results, Fig. 3 and Fig. 4 were obtained.

It is shown in the table that the amounts of vaporized n-octadecane are the same under constant conditions, even if added amounts are different. As in Fig. 3, it was ascertained that water vaporizes at a constant rate. Fig. 4 shows the relationship between the amount of vaporized water ( $W_w$ ) and that of vaporized n-octadecane ( $W_o$ ). In this case, a proportional relationship between them has been obtained and therefore the equation for steam distillation is considered applicable.

From this data,  $R (W_o/W_w)$  and the vapor pressure of n-octadecane were obtained as  $1.1 \times 10^{-3}$  and  $4.2 \times 10^{-2}$  (mmHg), respectively, by following the data analysis methods.

Furthermore, the ratio 'R' were compared under the different total pressures. As shown in Table 1, the evaporation experiments of the n-octadecane contaminated brine at a pressure of 500mmHg were carried out where other conditions were the same. As a result, R was obtained as  $1.3 \times 10^{-3}$  at the above pressure, that coincided well with that at 420mmHg. Therefore, it was ascertained that R does not change by different pressures if other



conditions are same.

### 5.3 Bromoform Carryover Test

In order to apply the equation for steam distillation to soluble contaminants, we developed a modified method as described in 'Appendix 2'. The demonstrations of this method were attempted in a 'Bromoform Carryover Test' and a follow-up 'Toluene Carryover Test'.

Bromoform is a kind of trihalomethane and is known to be often detectable in seawater and especially in chlorinated seawater of desalination plants at high concentrations. This is a highly soluble organic. It dissolves at 800 parts per million in pure water and in our observation the solubility in the brine was approximately 300mg/L. Therefore, in this study, bromoform was used as one of the typical soluble organics in order to establish the rule for the vaporization of these organics, when contaminating water (i.e. homogeneous system).

The evaporation experiments on the bromoform contaminated brine at about 0.4ppm were carried out by varying the vacuum time and the result obtained is as shown in Table 3. In these experiments, the concentration of bromoform remaining in the brine was measured with the PT-GC-ECD and corrected by calculating the initial concentration as 0.4ppm, following equation (5) in 'Appendix 2'.

Fig. 5 shows the relationship between the vacuum times and the bromoform concentrations in the brine ( $C_0$ ). The relationship between the vacuum times and the amounts of vaporized bromoform ( $W_0$ ) is presented in Fig. 6. It is obvious that the graphs obtained in these figures coincide well with the graphs that represent equation (5) and equation (6), presented in 'Appendix 2'. Therefore, the data analysis method described in 'Appendix 2' is considered applicable to the vaporization of soluble contaminants.

'R' is obtained as 0.11 (L/min.) from the slope of the graph in Fig. 7 which represents the relationship between the time and  $\ln C_0$ .  $V_w$  is obtained as 0.15 (mol./L min.) from the data in Table 3. By using these values, Henry's constant for bromoform at 90°C is calculated as  $3.7 \times 10^{-2}$  (mol./L. mmHg).

### 5.4 Toluene Carryover Test

Toluene is contained in crude oil as a major component and is soluble in water at a

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concentration of less than 500ppm. Therefore, in the case of oil spillage, it dissolves in seawater and may be sucked in by intakes of desalination plants.

In our experiments toluene concentration in the brine was approximately 2ppm where toluene was completely soluble in the brine. The result is presented in Table 4. The data were analyzed by the same method as that applied in 'Bromoform Carryover Test' and the results obtained are shown in Fig. 8 and Fig. 9. In this case, the shapes of these graphs are also fit well with equation (5) and equation (5') in 'Appendix 2'. Therefore, the data analysis method is also demonstrated to be applicable to the vaporization of soluble toluene.

$R'$  for toluene is obtained as 0.62. Thus, following the data analysis method, Henry's constant for toluene is calculated as  $2.1 \times 10^{-3}$  (mol./L, mmHg), that is a value 15 times lower than that of bromoform. This means that toluene is more volatile than bromoform.

### 5.5 Fuel Oil A Carryover Test

The experiments described above are concerned with various single contaminants. However, in considering an actual oil spillage, we recognize that the vaporization mechanism of a complex contaminant must be understood. In such a case, it is only natural to conclude that some modifications of methods are necessary in order to apply the rule established in the previous sections to the vaporization of a complex contaminant. Here, fuel oil A was used for this purpose.

The fuel oil A carryover test was carried out in the same manner as in the n-octadecane carryover test to measure the vaporized n-octadecane in fuel oil A. Table 5 shows the result of this experiment and the chromatography of residual components in the brine at different times are presented in Fig. 10 where all the major peaks are due to normal paraffins and the retention time of n-octadecane is 22.8 minutes. It can be observed in this figure that light components disappeared immediately and heavy components remained for longer periods.

Fig. 11 shows the relationship between the vacuum times and the weights of vaporized water, and Fig. 12 shows the relationship between the vacuum times and the weights of vaporized n-octadecane in fuel oil A. In Fig. 12, almost all n-octadecane in the added fuel oil A were vaporized by 25min. From these data, it was ascertained that the equation for steam distillation is applicable in this case, even if n-octadecane is one component of the

## (6.1.2)

complex contaminants.

The proportional constant in the equation for steam distillation,  $R$  ( $W_o/W_w$ ), for *n*-octadecane as a component of fuel oil A, can be seen in Fig. 13. In this case,  $R$  is obtained as  $2.7 \times 10^{-5}$ , although  $R$  for octadecane is  $1.1 \times 10^{-3}$  in the case where octadecane is the single contaminant. This shows that the vaporization rate of *n*-octadecane in a complex system is different from that in the single system and is reduced by approximately 40 times in the case of fuel oil A. This can be also ascertained by comparing the data in Ex. No.5-4 with Ex. No.5-13.

### 5.6 Bromoform-Fuel Oil A Mixture Carryover Test

When seawater is polluted by oily components, it is known that many trihalomethane are generated. Therefore, we must consider cases of complex pollution of seawater with oily components and trihalomethane. The purpose of 'Bromoform-Fuel Oil A Mixture Carryover Test' is to clarify the effect of contaminated fuel oil A on the vaporization of soluble bromoform.

Fuel oil A was added at a concentrations of approximately 20ppm and 200ppm and the vaporization of bromoform was carried out under the same conditions as the 'Bromoform Carryover Test'. The results are presented in Table 6.

In Table 6, the remaining bromoform was almost equal to that of the single contaminant, even in the case where 200ppm of fuel oil A was added. These results demonstrate that fuel oil A did not considerably affect the vaporization of bromoform.

## 6. Discussion

In this study, we carried out the evaporation experiments with the experimental batch evaporator on the brine in which some organics had been dissolved. As a result, it was shown that the vaporization of the insoluble contaminant, i.e. *n*-octadecane followed the equation for steam distillation. By using this equation, the amount of the vaporized contaminant can be obtained if the temperature and the amount of vaporized water is known. The temperature is necessary in order to obtain the vapor pressures.

In general, the vapor pressure is calculated by using Antoine's equation that has been

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described in the 'Background' section. However, this equation can usually be applied only to a certain range of temperature, for example the range of the temperature for the vapor pressure of n-octadecane which is from 173°C to 316°C. This time, in order to obtain the vapor pressure of n-paraffin, we applied the data obtained from Antoine's equation to Clapeyron-Clausius's equation, and the calculated result is presented in Fig. 14. Clapeyron-Clausius's equation is described below;

$$\ln P = - \frac{\Delta H}{RT} + \text{const.} \quad (\text{Clapeyron-Clausius's equation})$$

where P is the vapor pressure, T is the temperature, R is the gas constant and  $\Delta H$  is the Enthalpy.

From this method, the vapor pressure of n-octadecane at 90°C was calculated as  $6 \times 10^{-2}$  (mmHg). On the other hand, the vapor pressure obtained from the experiment is  $4.2 \times 10^{-2}$  (mmHg) which coincides well with the above value.

Following the equation for steam distillation, two important rules must be recognized. The first is that the ratio 'R' ( $W_o/W_w$ ) is not influenced by the total pressure of the vapor phase. This was demonstrated by the result in Table 2 where the evaporations were carried out at two pressures and comparisons were made of the 'R'.

The second is that the vaporization rates of insoluble contaminants are constant and independent of the amount in the brine. This is also demonstrated in Table 2 and therefore it is considered that insoluble contaminants vaporize at constant rates till all of them disappear. In this case, the amount of the vaporized contaminant ( $W_o$ ) is in proportion to time in the same way with the amount of vaporized water ( $W_w$ ).

However, soluble contaminants vaporize in a different manner. Concerned with the vaporization of soluble materials, Henry's law is well known. We established the data analysis method based on this equation.

As shown in Fig. 6, the vaporization of soluble materials follows the exponential function. Therefore, the vaporization rate depends on the concentration in the brine and they never disappear completely from the brine. This result shows that the data analysis method in Appendix 2 is the proper method for soluble contaminants. By using this method, if we obtain the concentration of the contaminant, the temperature of the evaporator and the

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vaporization rate of water ( $V_w$ ), the vaporization rate of contaminant ( $V_o$ ) can be calculated. However, Henry's constants for many organics have not been obtained, especially for trihalomethane. Therefore, it is necessary to measure Henry's constants for some trihalometane in a following study. In this case, we applied the following equation instead of the equation for steam distillation, because  $W_o$  could not be obtained only by multiplying  $V_o$  by time.

$$\frac{V_o}{V_w} = \frac{M_o \cdot C_o / H_o}{M_w \cdot P_w}$$

The vaporization of a complex contaminant was also studied in order to compare the vaporization rate of a component of a complex contaminant and the rate where the component existed singly. In the case of n-octadecane in fuel oil A, the vaporization rate was considerably affected and reduced by 40times, compared with the result of the singly n-octadecane carryover test.

In this case, it is considered that n-octadecane is one component of the solution, i.e., fuel oil A and modified Raoult's law that is described below is applicable to rule the vaporization:

$$p_i = x_i \cdot P_{oi} \cdot \gamma_i$$

where

- $p_i$  : the partial pressure of 'i' component,
- $x_i$  : the mole fraction of 'i' component
- $P_{oi}$  : the vapor pressure of the pure 'i' component
- $\gamma_i$  : the activity coefficient of 'i' component

From this equation and the modified equation for steam distillation, the following equation is obtained that rules the vaporization of a complex contaminant.

$$\frac{V_{oi}}{V_w} = \frac{M_{oi} \cdot P_{oi} \cdot x_i \cdot \gamma_i}{M_w \cdot P_w}$$

The mole fraction of n-octadecane is calculated as approximately 0.02 from the data of gas chromatography. Therefore, when the activity coefficient is supposed to be 1, R ( $V_{oi}/V_w$ ) for n-octadecane in fuel oil A is obtained as  $2.1 \times 10^{-5}$ . This coincides well with the value obtained from the experiment that is  $2.7 \times 10^{-5}$  and if we take a more accurate value of the

(6.1.2)

activity coefficient into consideration, we may calculate it more accurately.

On the other hand, a considerable effect of fuel oil A on the vaporization of bromoform was not observed. The reason is thought that the mass of fuel oil A was too small to transfer a considerable amount of bromoform in the brine. Therefore, in the case of an actual oil spillage, it is also thought that the vaporization of soluble contaminants is not affected greatly by the spilled oil.

As described above, we carried out 'Oil Carryover Test' and defined the basic rules of the vaporization mechanism of some contaminants in the brine. However, taking the actual MSF plants into consideration, we realized the necessity of further studies on the condensation mechanism of vaporized materials in order to anticipate the quality of the product water.

## 7. Conclusion

The SWCC-JICA collaborative research, MSF-2 has been conducted for the purpose of establishing methods to predict the level of the product water contamination during oil pollution in seawater. Oil Carryover Test is the starting point of this research and we attempted to clarify the basic rules for the vaporization mechanisms of some organics contaminated in the brine. The results of this study are summarized as follows:

- 1) We demonstrated that the equation for steam distillation (1) was applicable to the evaporation of high molecular weight hydrocarbons with n-octadecane which is barely soluble in the brine.

$$\frac{W_o}{W_w} = \frac{M_o \cdot P_o}{M_w \cdot P_w} \dots\dots\dots (1)$$

Following this equation, if we know  $W_w$  which is the amount of vaporized water, the amount of vaporized contaminant ( $W_o$ ) can be obtained.

- 2) We studied the vaporization of bromoform and toluene, and developed a modified equation (2) that could apply to the vaporization of not only insoluble contaminants (heterogeneous system) but also soluble contaminants (homogeneous system);

(6.1.2)

$$\frac{V_o}{V_w} = \frac{M_o \cdot C_o / H_o}{M_w \cdot P_w} \dots\dots\dots (2)$$

where V is the vaporization rate.

- 3) We studied the vaporization of complex contaminants by using fuel oil A. In this study, the vaporization rate of n-octadecane was reduced by approximately 40 times, compared with that of the single system, and then it was considered that Raoult's law could be applied to this case and following equation (3) was proposed:

$$\frac{V_{oi}}{V_w} = \frac{M_{oi} \cdot P_{oi} \cdot x_i \cdot \gamma_i}{M_w \cdot P_w} \dots\dots\dots (3)$$

In this study, it was concluded that this equation should be applied to the basis of the following computer simulation studies.

- 4) We examined influences of contaminated fuel oil A on the vaporization rate of bromoform. In our experiments, the influence was negligible.

Based on the above results, further studies on the following issues are necessary to establish the computer simulation methods;

1. to clarify and formulate the condensation mechanism of vaporized materials,
2. to prepare the constants that are required in the computer simulation study.

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(6.1.2)

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## Appendix 1

### The basic procedure of 'Oil Carryover Test'

#### 1. Preparations Part-1

- 1-1. Set up the test unit as presented in Fig. 1. Set these in a draft if possible.
- 1-2. Measure the time that has elapsed by raising the temperature of the brine in the flask to the desired temperature.
- 1-3. Determine the volume of the solvent in the impinger. Make sure that the volume does not decrease at vacuum conditions.
- 1-4. Prepare the brine (add 41g NaCl and 30g Instant Ocean in 1 liter water).
- 1-5. Check the quality of the solvent used for extraction with gas chromatography (ex. CCl<sub>4</sub>, n-Hexane).

#### 2. Preparations Part-2

- 2-1. Start the flow of cooling water (15~20°C) in the condenser.
- 2-2. Set the waterbath. Adjust the temperature of the water bath 2 or 3 degrees higher than desired.
- 2-3. Wash the inside of the test unit. Enter Ca. 50ml of acetone into the flask and evaporate it according to certain conditions (Close the valve at the condenser section. Use an aspirator.). When acetone in the flask is lost, stop the evaporation and discard all solvents in the implements. Next, add the solvent for extraction into the flask, and repeat the entire procedure. Then, dry the inside of the test unit by using a heat gun.
- 2-4. Set the impinger. Add a certain amount of the solvent, and set the impinger into the ice bath. Add NaCl to the icebath and adjust the temperature to between -5~-10°C.

### **3. Evaporation**

**Attention : All experimental apparatuses should be washed with the extraction solvent and dried.**

#### **3-1. Prepare the sample in the flask.**

- (1) Add 500ml of the brine to the flask and measure the weight.**
- (2) Suck the organics used as the contaminant into a microsyringe and cap with a piece of silicon.**
- (3) Measure the total weight of the microsyringe.**
- (4) Add a certain amount of the organics to the brine.**
- (5) Measure the total weight of the microsyringe and the remaining organics.  
\*Calculate the weight of the hydrocarbon poured into the flask.**
- (6) Set the flask to soak in the bath.**
- (7) Start to rotate the flask at 50rpm and close the valve.  
\*Wait for 10min. (It takes about 10min. for the temperature of the brine to reach the desired temperature.)**

#### **3-2. Start to vacuum.**

**\*Be careful that the solvent in the impinger does not decrease.**

#### **3-3. After reaching the desired pressure, start to measure the time (from 0min.).**

#### **3-4. When the desired time elapses, open the valve slightly and then stop the vacuum pump.**

**\*Be careful that the solvent in the impinger does not decrease.**

#### **3-5. Remove the flask, cap it and cool it in water. Measure the weight of this flask.**

#### **4. Recovery of the contaminants**

##### **4-1. Recovery from the condenser.**

Set up the new flask containing 30ml of the extraction solvent (ex.  $\text{CCl}_4$ ). Evaporate the solvent with rotating and evacuating according to certain conditions. The solvent should be recovered in the round-bottom flask in the condenser section. Transfer the solvent to a measuring flask. Wash the flask with some of the solvent and transfer it to the measuring flask. Add the solvent and increase the volume to 50ml. Add 5g of  $\text{Na}_2\text{SO}_4$  to the measuring flask and shake it.

##### **4-2. Recovery from the impinger.**

Remove the impinger from the test unit and transfer the solvent to a measuring flask. Wash the inside of the impinger with some of the extraction solvent, then transfer it to the measuring flask. Increase the volume in the measuring flask to 50ml. Add 5g of  $\text{Na}_2\text{SO}_4$  to the measuring flask and shake it.

##### **4-3. Recover the remainings in the flask**

Add 50ml of the extraction solvent and shake it for 5 minutes. Let it stand it for a while and recover the solvent fraction with a pipette. Add 5g of  $\text{Na}_2\text{SO}_4$  to the measuring flask and shake it.

## Appendix 2

### Data Analysis Methods

#### 1. Insoluble System (Heterogeneous System)

The data on 'n-octadecane carryover test' and 'Fuel oil A carryover test' are plotted on graphs where x-axis represents  $W_w$  and y-axis represents  $W_o$ . If we obtain a proportional relationship between them as we have below, then it is assumed that the equation for steam distillation is applicable to these cases.

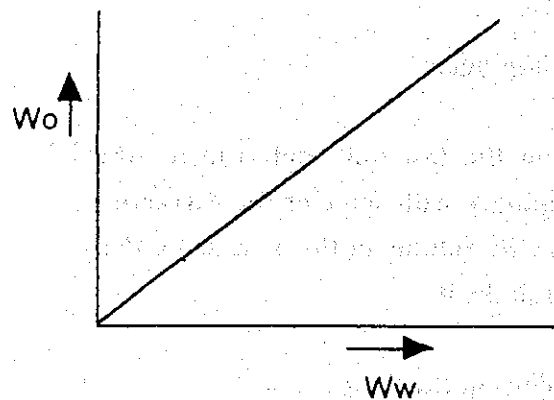


Fig. The relationship between  $W_o$  and  $W_w$  in an insoluble system

The proportional constant ( $R$ ) is obtained from the graph. Compare  $R$  of the single n-octadecane and  $R$  of n-octadecane in fuel oil A.

By following the equation for steam distillation, the vapor pressure of nC18 at  $90^\circ\text{C}$ , is calculated from the result of 'n-octadecane carryover test, as below.

$$P_{nC18} = \frac{R \cdot M_w \cdot P_w}{M_{nC18}} = \frac{R \times 18 \times 526}{254} = 37.3R$$

#### 2. Soluble System (Homogeneous System)

When the vaporization rates of a soluble contaminants and water are represented as  $V_o$  and  $V_w$ , respectively, the equation is rewritten as below:

$$\frac{M_o \cdot P_o}{M_w \cdot P_w} = \frac{W_o}{W_w} = \frac{V_o \cdot t}{V_w \cdot t} = \frac{V_o}{V_w} \dots\dots\dots (1)$$

In this equation,  $M_o$ ,  $M_w$ ,  $P_w$  are the constants and as per the previous experiments  $V_w$  is also considered as a constant. However,  $P_o$  for solubilized materials is known to be ruled by Henry's law (equation (2));

$$C = HP \dots\dots\dots (2)$$

where  $C$  is the concentration of the solubilized material,  $H$  is Henry's constant and  $P$  is the vapor pressure of the material. Therefore, when  $C_o$  changes by time,  $P_o$  becomes a function against time and equation (1) is rewritten as below;

$$V_o(t) = R \cdot P_o(t) = R/H \cdot C_o(t) = R' \cdot C_o(t) \dots\dots\dots (3)$$

where  $R$ ,  $R'$  are the constants. Therefore the concentration of the contaminants in the water at time 'x' is as follows.

$$\begin{aligned} C_o(x) &= C_o(0) - \int_0^x V_o(t) dt \\ &= C_o(0) - \int_0^x R' \cdot C_o(t) dt \dots\dots\dots (4) \end{aligned}$$

From this differential equation, we obtain equation (5) and (5').

$$C_o(t) = C_o(0) \cdot e^{-R' t} \dots\dots\dots (5)$$

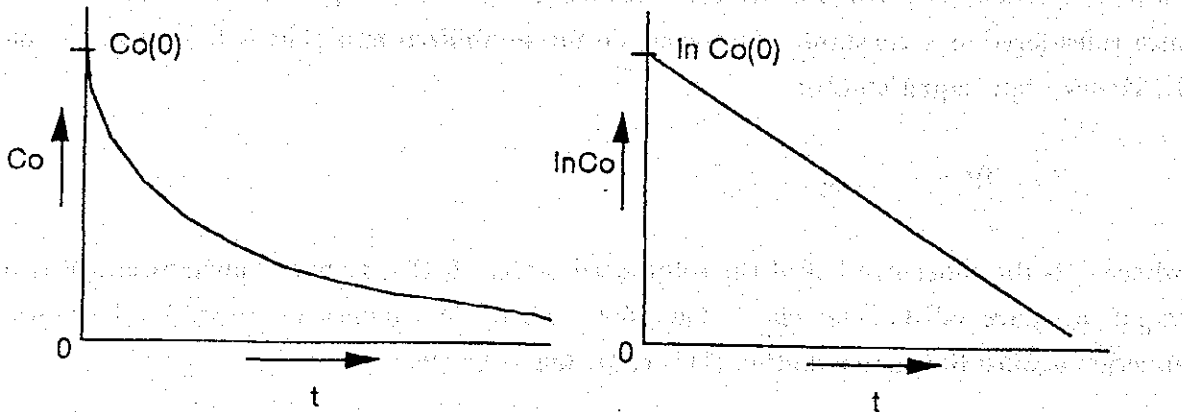
$$\ln C_o(t) = \ln C_o(0) - R' t \dots\dots\dots (5')$$

By applying this equation to equation (1) and (2),  $W_o(t)$  is obtained as follows;

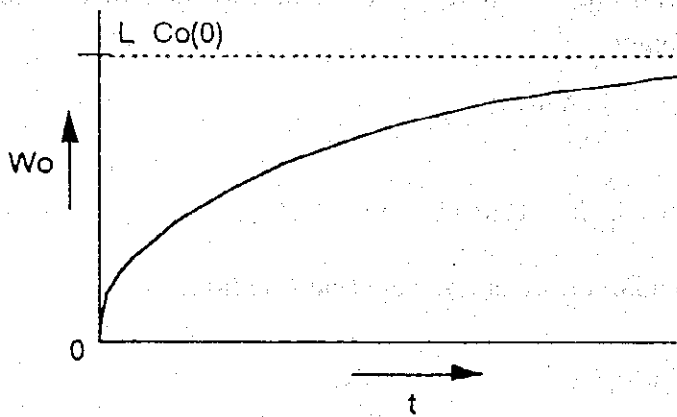
$$W_o(t) = L \cdot C_o(0) \cdot (1 - e^{-R' t}) \dots\dots\dots (6)$$

where  $L$  is the volume of the brine.

Equation (5), (5') and equation (6) are considered to represent graphs, shown in Fig. 1 and Fig. 2, respectively.



**Fig. 1 Theoretical Relationship between t and Co**



**Fig. 2 Theoretical Relationship between t and Wo**

In an experiment,  $C_o$  is measured by changing time, and a graph that represents the relationship between  $t$  and  $C_o$  is made. If this graph fits equation (5) or (5'), it is then demonstrated that equation (1) is applicable to soluble contaminants. In this case, Henry's constant is calculated as follows.

$$H = \frac{M_o \cdot V_w}{M_w \cdot P_w \cdot R'} \quad (\text{mol/l mmHg})$$

## (6.1.2)

**Table 1 The result of Material Balance Experiment**

Ex. No.	Conditions	Recovery(%)*			
		Flask	Condenser	Impinger	Total
1-1	nC18 ,10ppm, 90°C	30	61	-	91
1-2	,50ppm, 90°C	84	18	1	102
1-3	,50ppm, 40°C	112	<1	<1	112
1-4	nC8 ,10ppm, 90°C	-	2	92	94
1-5	,50ppm, 90°C	1	1	95	97
1-6	,50ppm, 40°C	19	1	83	102
1-7	CHBr3,10ppm, 90°C	48	2	40	90
1-8	,10ppm, 40°C	85	1	12	97

**\*Recovery(%)=(The weight of hydrocarbons measured with GC after the evaporation / The initial weight added in the brine) x 100**

(6.1.2)

**Table 2 The Result of n-Octadecane Carryover Test**

Ex. No.	Time(min)	Vaporized Water(g) (Ww)	nC18(mg)		
			Initial	Remained	Vaporized (Wo)
2-1	0	1	9	10	-
2-2	10	14	33	16	17
2-3	20	21	30	7	23
2-4	5	6	33	25	8
2-5	5	7	30	24	6
2-6	10	10	19	7	12
2-7	10	11	47	34	13
2-8	10	8	20	11	9
2-9	10	9	12	4	8
2-10	30	32	42	13	33
2-11	10	1.4	21	19	2
2-12	20	3.3	19	15	4

Ex. No.2-11 and Ex. No.2-12 were carried out at the pressure of 500mmHg. The conditions of other experiments were described in Materials and Methods.



(6.1.2)

**Table 3 The Result of Bromoform Carryover Test<sup>(1)</sup>**

Ex. No.	Time(min.)	Vaporized Water(g)	Bromoform(ppb)		
			Initial	Remaining	Corrected <sup>(2)</sup> (Co)
3-1	10	12.8	420	75	72
3-2	20	27.0	400	38	38
3-3	30	41.9	461	11	10
3-4	0	1.0	353	297	336
3-5	5	7.3	358	119	133
3-6	15	18.8	369	46	43
3-7	10	10.7	362	69	76
3-8	12	15.8	357	56	62
3-9	7	9.2	359	82	92
3-10	3	4.9	274	149	218

- (1) The experimental Conditions are described in Materials and Methods.
- (2) This value was calculated by correcting the initial concentration as 400ppb.

(6.1.2)

**Table 4 The Result of Toluene Carryover Test<sup>(1)</sup>**

Ex.No.	Time(min)	Vap.Water Ww(g)	Toluene Conc.(ppm)		
			Initial	Remaining	Corrected <sup>(2)</sup> Co(t)
4-1	0	0.8	2.34	1.43	1.22
4-2	5	6.5	2.25	0.05	0.04
4-3	3	4.2	2.39	0.24	0.20
4-4	2	2.7	2.42	0.37	0.31
4-5	4	4.8	2.27	0.14	0.12
4-6	1	1.7	2.07	0.58	0.56

(1) The experimental conditions are described in Materials and Methods.

(2) This value was calculated by correcting the initial concentration as 2ppm.

(6.1.2)

**Table 5 The Result of Fuel Oil A Carryover Test<sup>(1)</sup>**

Ex. No.	Time(min)	Added Fuel Oil A (mg)	Vap. Water, Ww (g)	nC18(mg)		
				Initial	Remaining	Vaporized
5-1	10	62	12.0	0.99	0.67	0.32
5-2	10	21	11.1	0.34	0.04	0.30
5-3	10	13	10.0	0.21	<0.01	0.21
5-4	10	97	11.6	1.55	1.27	0.28
5-5	0	61	0.5	0.98	0.92	0.06
5-6	5	62	6.7	0.99	0.81	0.18
5-7	20	57	21.0	0.92	0.14	0.78
5-8	30	59	34.0	0.94	0.14	0.80
5-9	60	58	57.3	0.93	0.03	0.90
5-10	40	60	47.1	0.96	0.02	0.94
5-11	25	56	32.2	0.90	0.03	0.87
5-12	15	54	18.0	0.86	0.24	0.62
5-13 <sup>(2)</sup>	10	-	10.7	1.6	<0.01	1.6

- (1) The experimental conditions are described in Materials and Methods.
- (2) In this experiment, pure n-octadecane was used as the single contaminant.

(6.1.2)

**Table 6 The result of Bromoform-Fuel Oil A Mixture Carryover Test\***

Ex.No.	Added Fuel Oil A (mg)	Vap. Water(g)	Bromoform(ppb)		
			Initial	Remaining	Vaporized
6-1	0	9.9	357	65	292
6-2	12	12.4	383	84	299
6-3	13	10.8	362	91	271
6-4	98	11.5	358	91	267
6-5	108	12.3	375	85	290

(1) The experimental conditions are described in Materials and Methods:

(6.1.2)

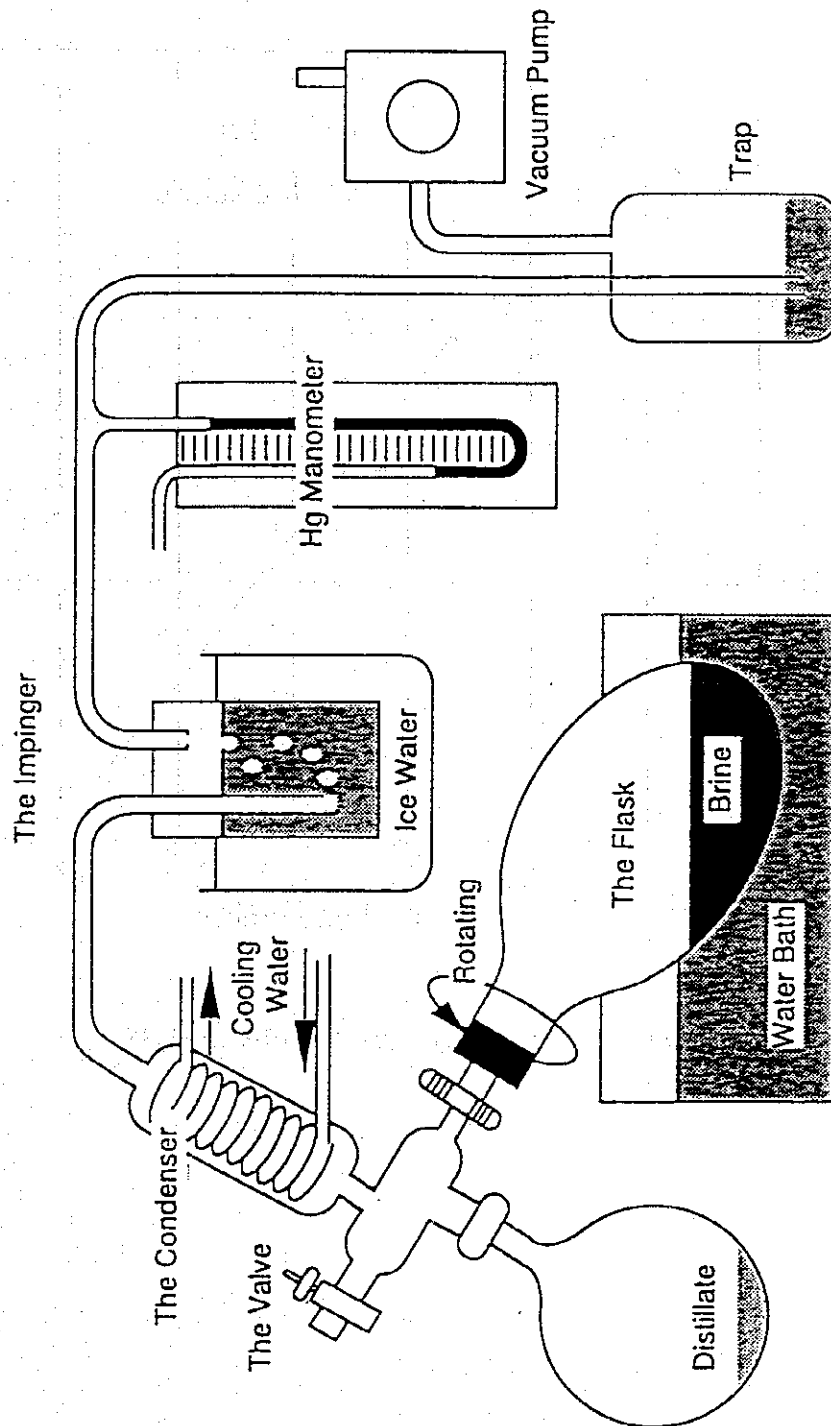


Fig. 1 Schematic Diagram of Oil Carryover Test Unit

(6.1.2)

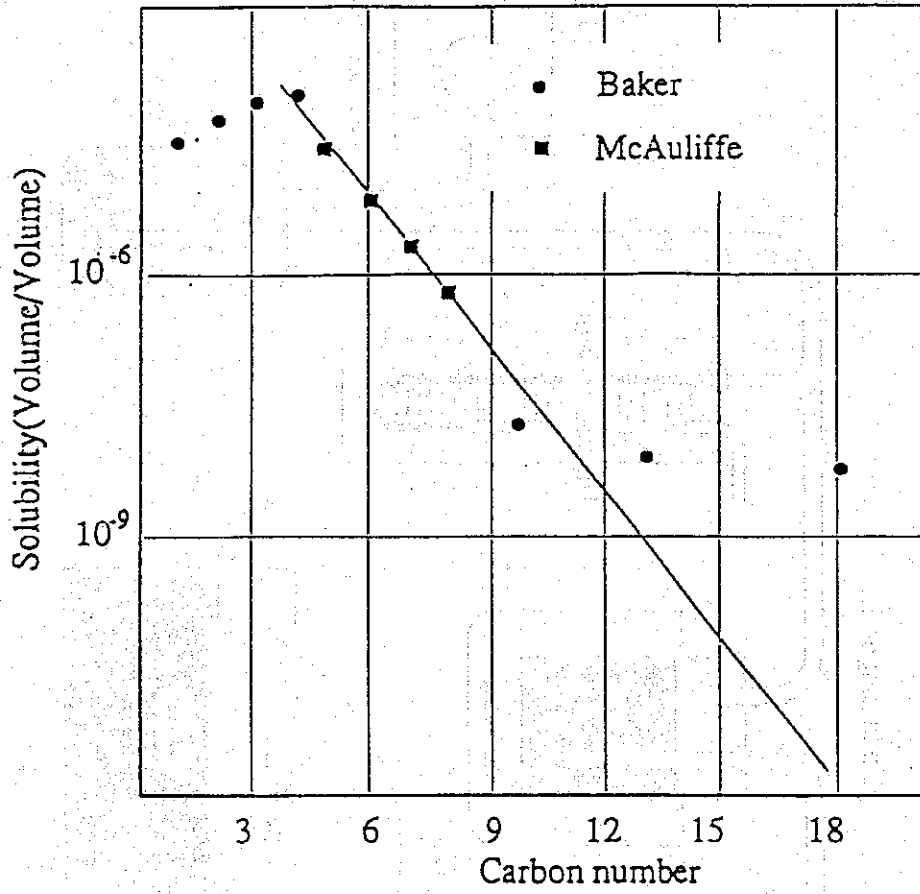
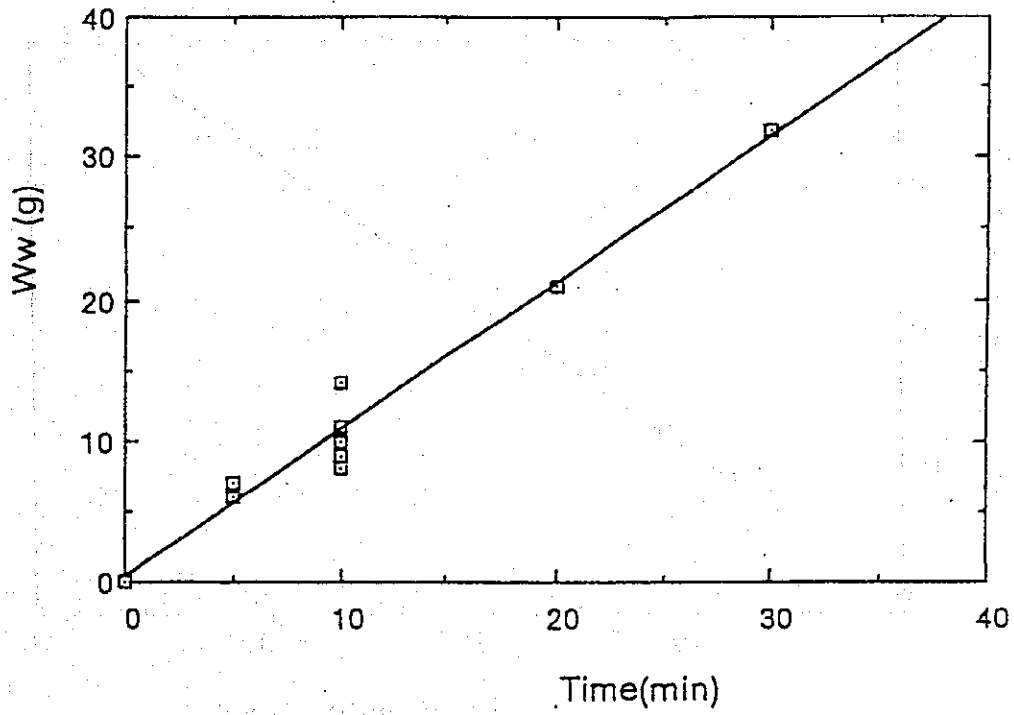


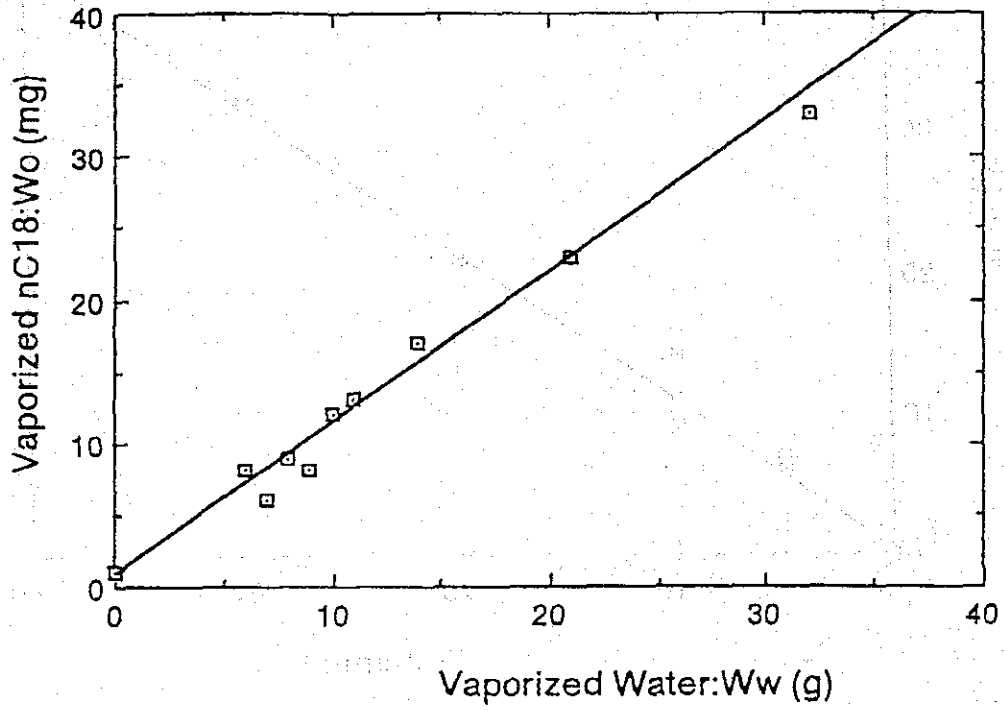
Fig. 2 Solubility of n-Paraffins in H<sub>2</sub>O

(6.1.2)



**Fig. 3 The Relationship between Vaporization Time and the Amount of Vaporized Water in n-Octadecane Carryover Test**

(6.1.2)



**Fig. 4** The Relationship between Vaporized Water and Vaporized n-Octadecane in n-Octadecane Carryover Test



(6.1.2)

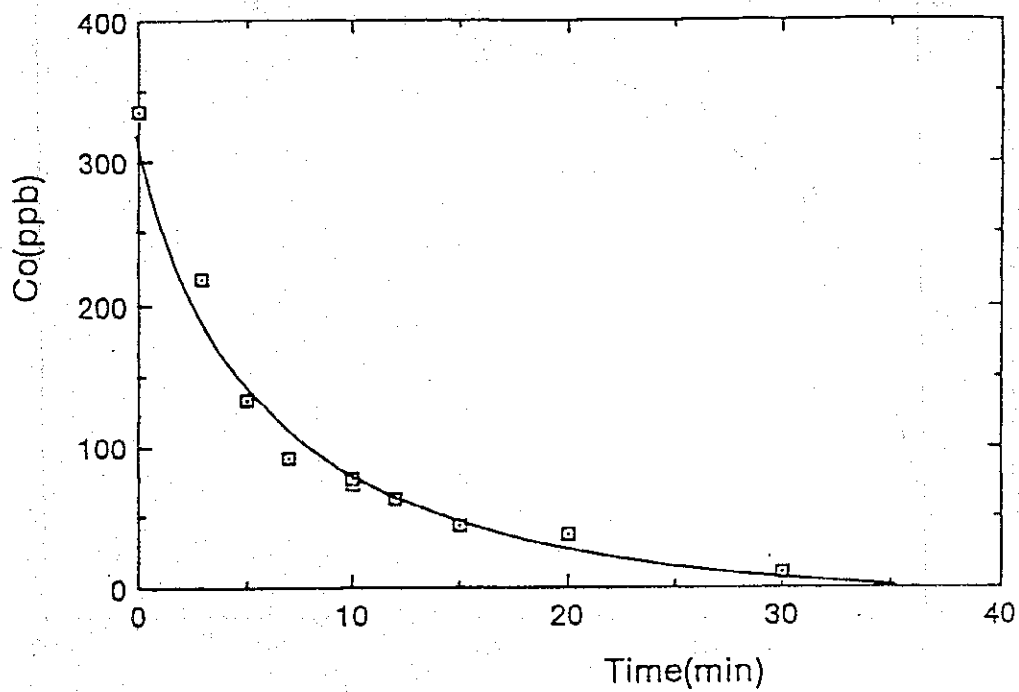


Fig. 5 Time Course of the Bromoform Concentration in the Brine

(6.1.2)

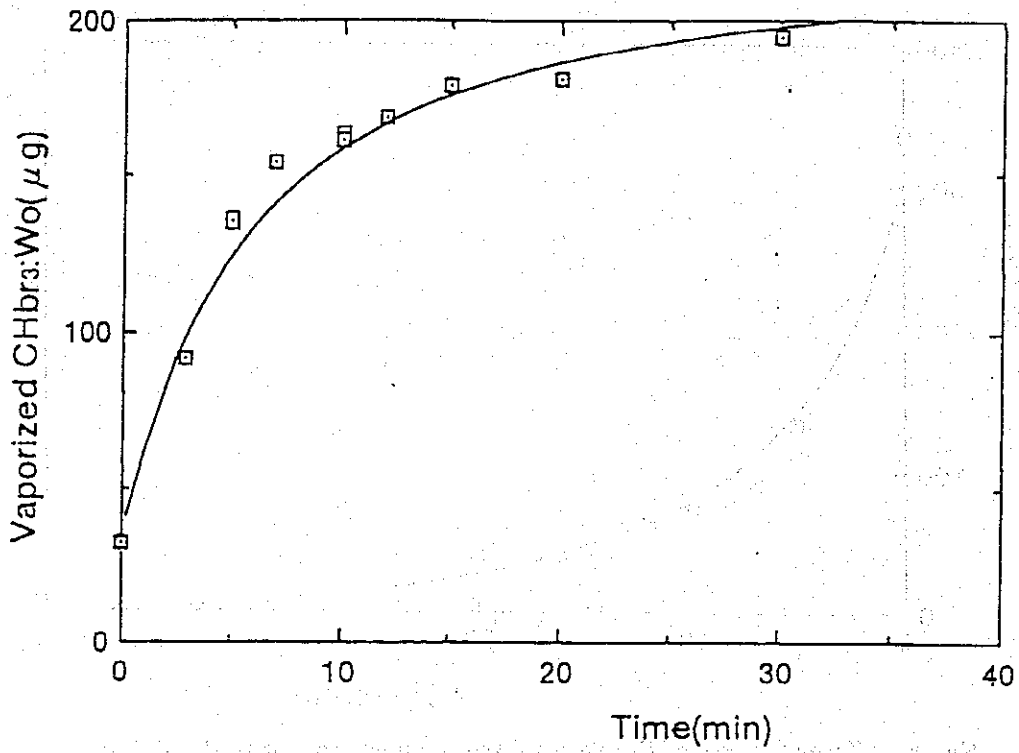
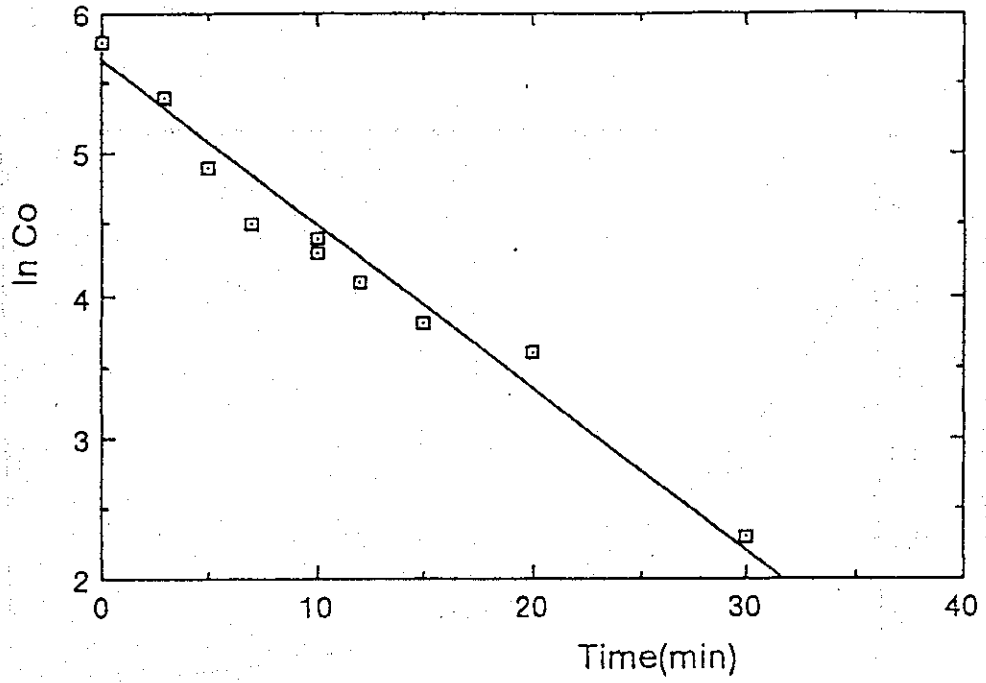


Fig. 6 Time Course of the Amount of Vaporized Bromoform

(6.1.2)



**Fig. 7** The Relationship between the Time and ln Co in Bromoform Carryover Test

(6.1.2)

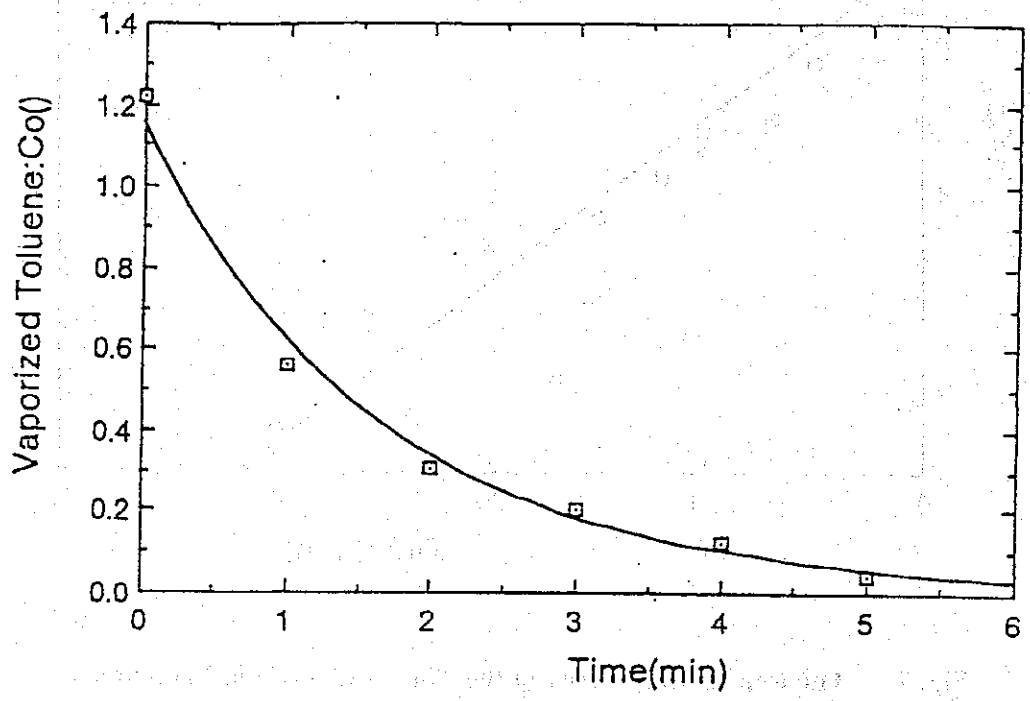
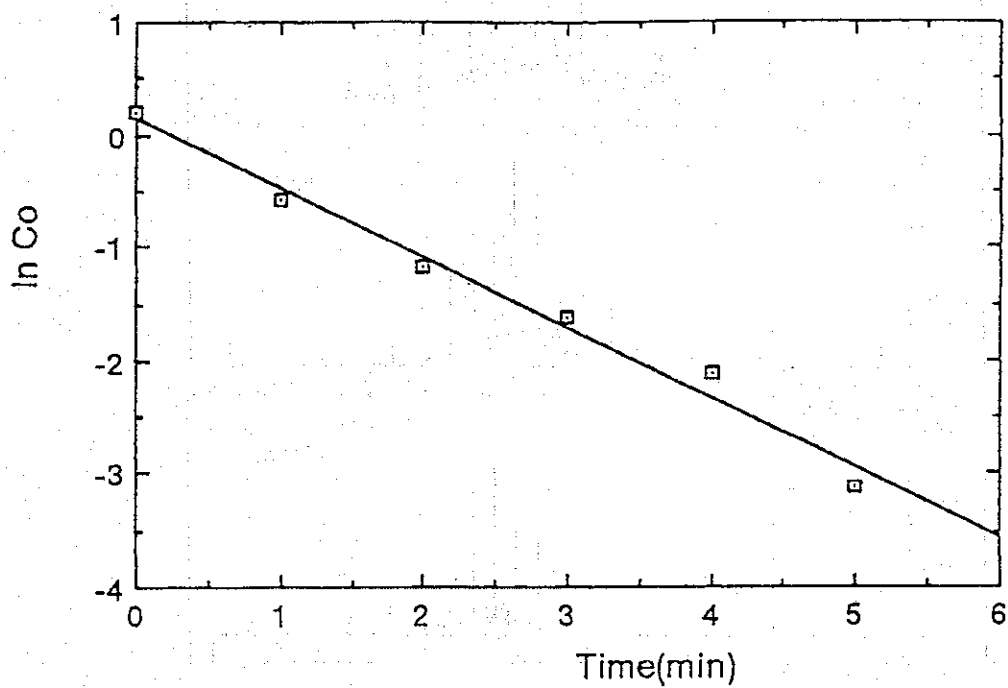


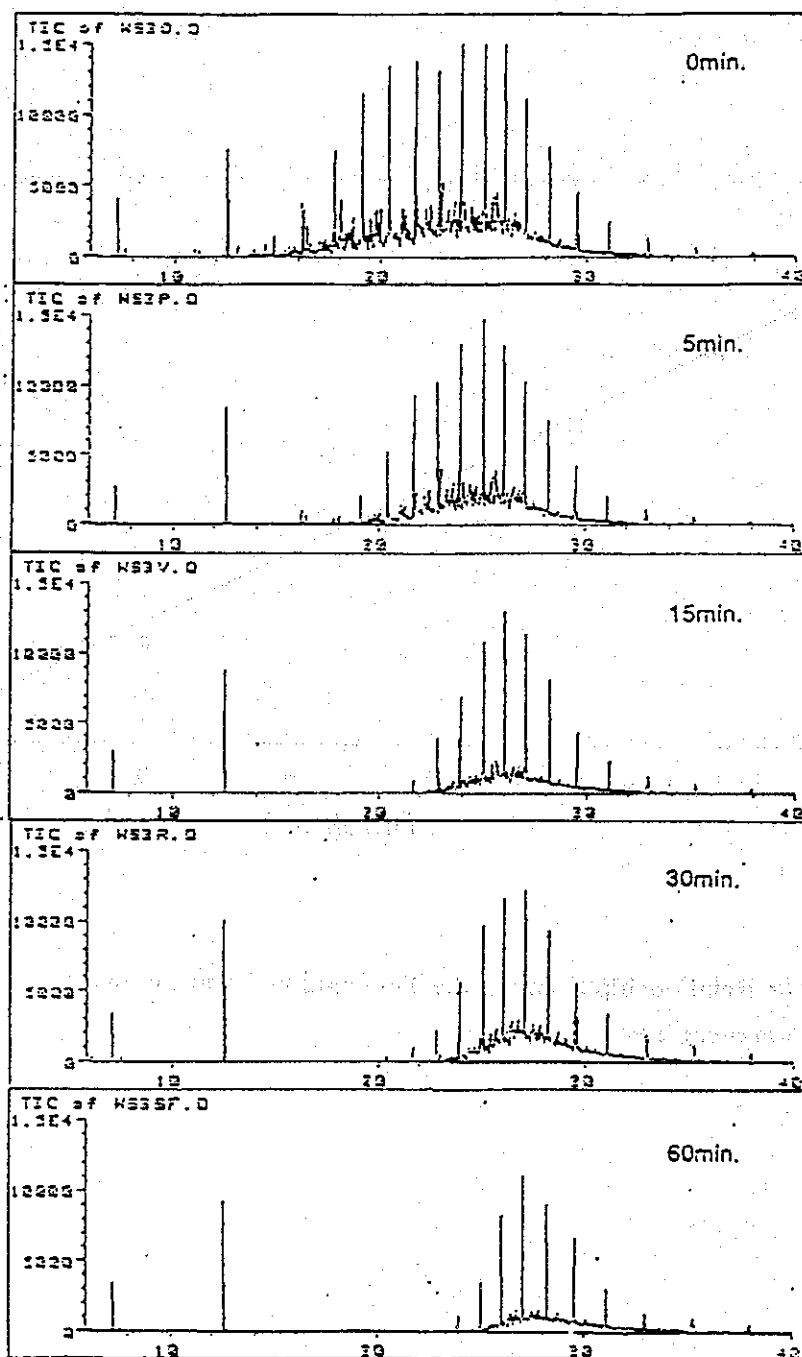
Fig. 8 Time Course of the Toluene Concentration in the Brine

(6.1.2)



**Fig. 9** The Relationship between the Time and ln Co in Toluene Carryover Test

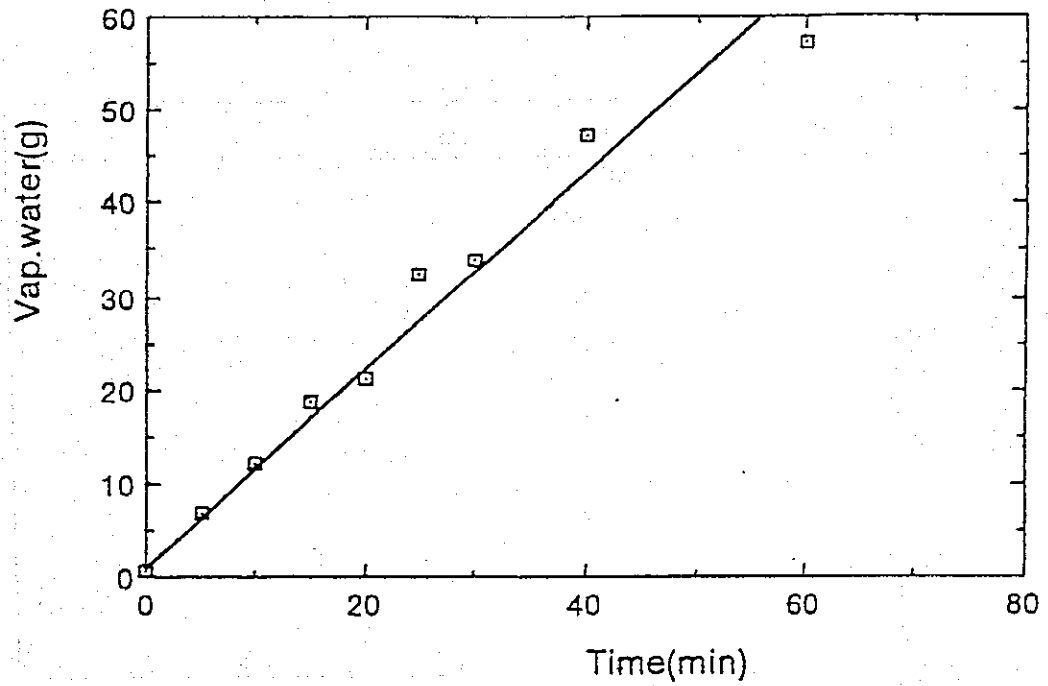
(6.1.2)



The retention time of the octadecane peak is 22.8min.  
The two big peaks appeared at 7.5min. and 12.5min. are due to the impurities of CCl<sub>4</sub>.

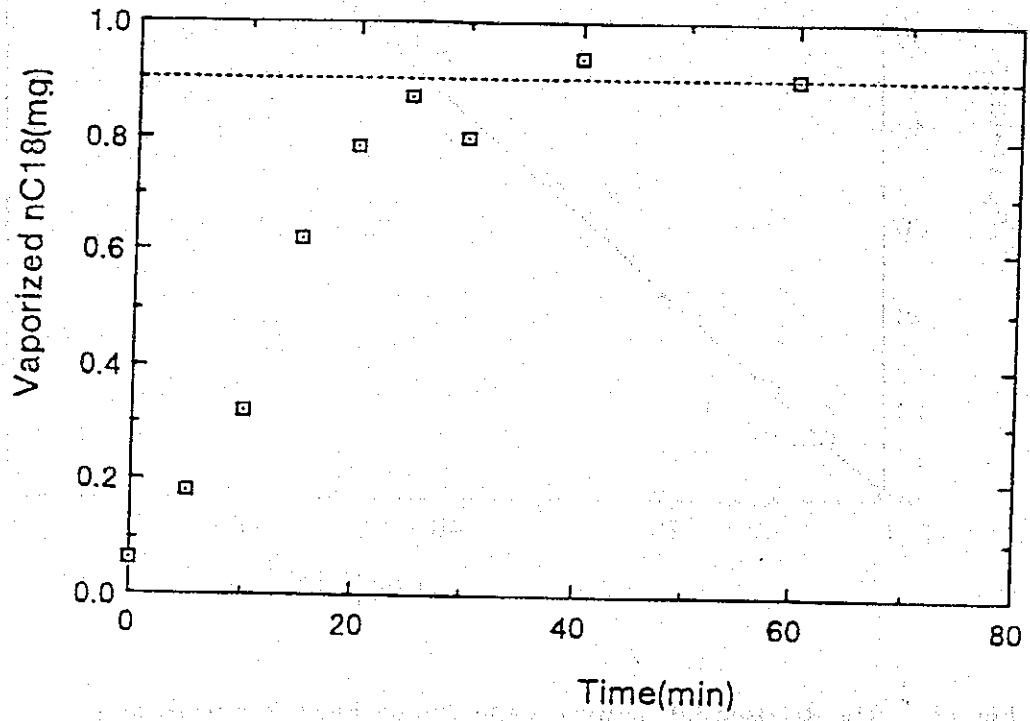
**Fig. 10 Chromatograms of Residual Components in the Brine at Different Evaporation Times**

(6.1.2)



**Fig. 11 The Relationship between Vaporization Time and the Amount of Vaporized Water in Fuel Oil A Carryover Test**

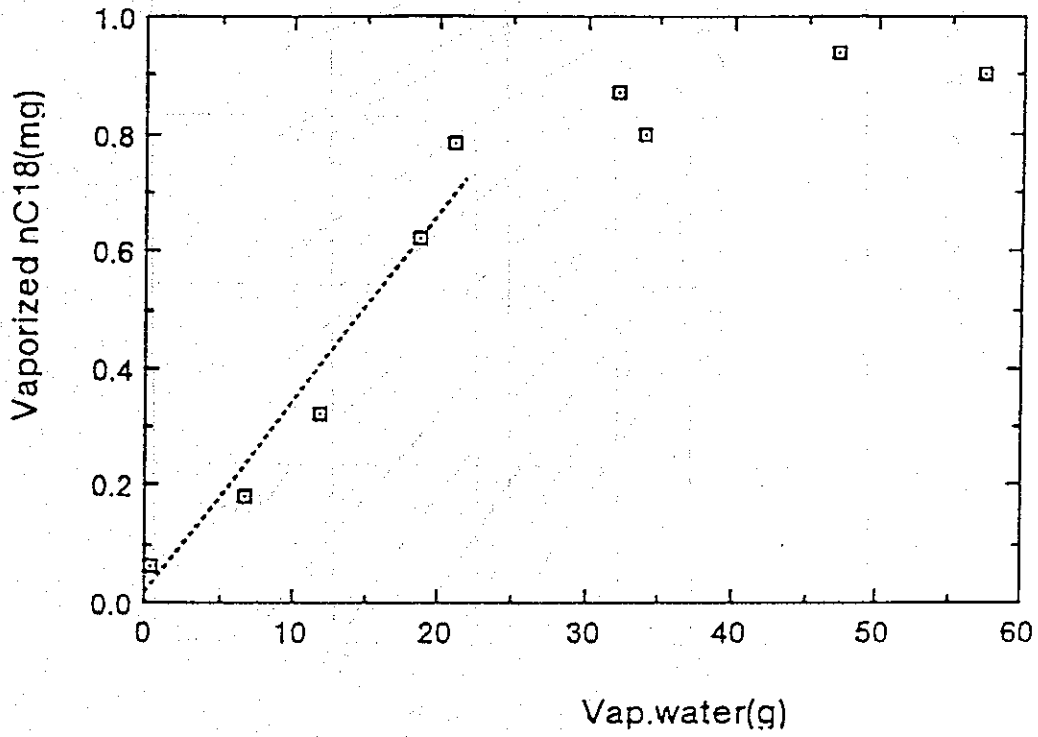
(6.1.2)



**Fig. 12 The Relationship between Vaporization Time and the amount of Vaporized n-Octadecane in Fuel Oil A Carryover Test**



(6.1.2)



**Fig. 13** The Relationship between vaporized Water and Vaporized n-Octadecane in Fuel Oil A Carryover Test

(6.1.2)

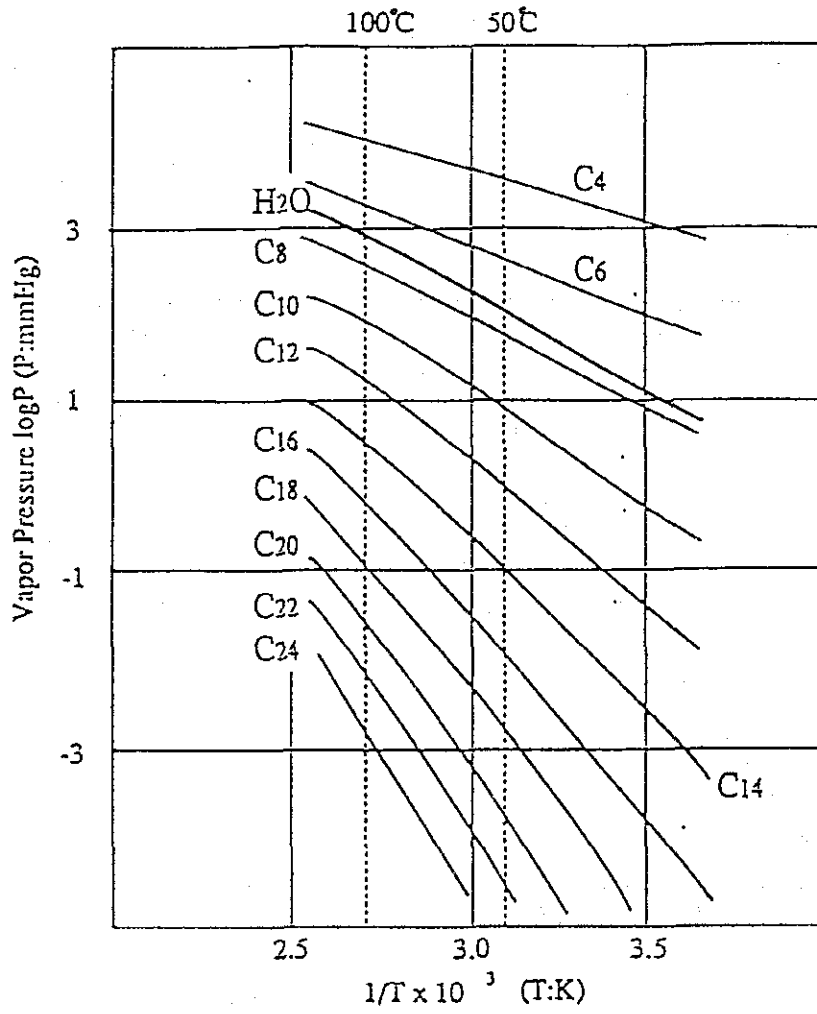


Fig. 14 Vapor Pressure of n-Paraffin

## **6.2 Measurement of Vapor-Liquid Equilibria**



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## **1. Introduction**

For the purpose of predicting the product water quality in the event of seawater pollution the first step of MSF-2 project aims at the estimation of carryover of oil from MSF brine, when the seawater containing the escaped crude oil is fed to the MSF test plant as the make up water.

To have an understanding of the carry over process a computer program for the quantitative estimation of the vaporized contaminants in brine was developed, based on the data obtained from the vaporization mechanism of organic contaminants using a typical fuel and bromoform conducted as the primary experiments. These data are shown in 6.1.2.

During the reported period an extended study was conducted to determine Henry's Constant using a vapor-liquid equilibrium apparatus. Results of the experiment with this apparatus is expected to improve the reliability of the above mentioned computer program.

To estimate a reliable Henry's Constant it is necessary to establish an equilibrium condition between gas phase and liquid phase under the vaporizing system of seawater or brine in which oil constituents exist heterogeneously and also in which a soluble organic compound such as bromoform, which is the major constituent of trihalomethane, exists homogeneously.

The results of the experiment with bromoform selected as a typical organic contaminant to provide a homogeneous system and using the vapor-liquid equilibrium apparatus are described here. The data is expected to be used, in general, for other organic contaminants.

As has been mentioned above, the experiment with vapor liquid equilibrium apparatus was carried out in order to improve the reliability of the formula developed for the computer program, by way of obtaining values for Henry's constant for bromoform which is most important in the equilibrium relation between gas and liquid phases, and also for the comparison of the new results with the results obtained from the preliminary experiments using different apparatus and technique.

## **2. Experimental Plan**

To determine Henry's constant by calculation from experimental data on equilibrium concentration, a vapor-liquid equilibrium apparatus model R-W type was used and is

shown in Fig. 1. Vapor liquid equilibrium apparatus essentially consist of three parts (A) Vapor/Liquid Equilibrium system, (B) Operation control panel (C) Vacuum/Exhaust system. Specification details are given in Table 1. Experimental details are as follows:

## 2.1 Experimental Procedures:

### 2.1.1 Leak Test

Vapor Liquid equilibrium apparatus model (R-W) was used for obtaining the equilibrium concentration of bromoform in gas and liquid phase. After connecting the apparatus as shown in Fig. 1., additional traps were put between points No.25 (of main equipment) and No.1 (of exhaust unit) to collect any uncondensed vapor escaping from condensing column. Uncondensed vapors were allowed to pass thorough traps filled with H<sub>2</sub>O or Haxane to collect bromoform. A leak test was carried out before the actual measurements. The procedure followed for leak test is given below. Initially all the change over cocks (No.20,21,22,23 in Fig. 1) are brought to such a position that they isolate the open end to atmosphere. All the change over glass cocks (also used for sample collection) are closed. Ice cubes are placed in flask (No.13) for safety of the pump. Instrument is connected to main power line through stabilizer (100 v output). Switches No.17 and 3, on measurement operation panel and vacuum exhaust system, respectively, are switched on. To control the vacuum, two contact points SP1 & SP2 are set at 50 and 51 mm Hg. Now switch No.6 (Fig. 1) is put on and leak valve No.7 is closed and streaming control valve No.8 is opened slowly and simultaneously.

One will be able to see the pressure reading on panel and when set point pressure SP1 & SP2 is attained, pump trips out and pressure is maintained automatically by vacuum control switch (No.4). When pressure of 50 mm Hg was attained the streaming control valve No.8 was also closed and pressure drop was monitored at end of 0,2,5,10,15 min. initially and there after at interval of 15 min. up to a period of 3 hrs. Graph of pressure versus time was plotted to get leakage curve. The vacuum was found to maintain up to a duration of 120 min. which is well over the experimental duration of 90-100 minutes.

### 2.1.2 Equilibrium Studies for Bromoform

To carry out equilibrium tests at different temperatures and pressures as per the schedule discussed in earlier section, pressures are set at (SP1 and SP2) required values as per

temperature requirement which can be noted from steam tables. All connection and cocks are set as discussed in leak test and vacuum pump is operated. When desired vacuum as per SP1 and SP2 set points is achieved, seawater samples containing bromoform is introduced in the system. Seawater samples containing either 10 or 100 ppm of bromoform were prepared as follows:

Seawater from Arabian Gulf was first filtered through filter paper No.1. A weighed quantity of bromoform was taken in standard flask and then filtered seawater is added to same flask, stoppered and shaken for 30-45 min. on a magnetic stirrer till all the bromoform get dissolved in seawater. When no more bubbles of bromoform are seen in samples, an aliquote of the sample is taken and analyzed. 275 ml of sample containing Bromoform is poured into sample supply column (No.6 of Fig. 1) by opening upper stopper while keeping the stop cock closed as set vacuum is already achieved in the remaining part of apparatus. Then stop cock is opened so that sample can be transferred to equilibrium unit (No.5 of Fig.1). After total transfer of sample from supply column stop cock of the column is closed. Desired pressure is monitored on exhaust unit and if pressure monitored is same as set value, cock No.19 of equilibrium unit and valve No.8 exhaust system is closed. Temperature of sample in equilibrium unit (No.5) is raised with help of still heater No.3. Similarly, heaters No.1 and No.2 are also switched on. When temperature in unit No.5 reaches to boiling point at the set pressure (SP1 & SP2), liquid and vapor are transferred to unit No.4 and equilibrium is monitored. Some vapor pass through condensing column No.7 and get accumulated there after condensation. Thus at a fixed set pressure of SP1 & SP2 and temperature, equilibrium is achieved at various places between vapor and liquid phases. 60-90 min. after equilibrium is achieved samples were collected from different sample collecting points (No.9,10,11,12) and from traps. These samples thus collected were analyzed and quantified by gas chromatographic techniques. Purge trap auto-injector (Model LSC-2 Tekmar, U.S.A.) in conjunction with gas chromatography (model 5880, Hewlett Packard U.S.A.) with an electron capture detector was used. Samples were diluted to adjust the bromoform concentrations in 1-10 ppb range where the GC response was found to be linear with respect to concentration.

## 2.2 Calculation of Henry's Constant using the Obtained Data

Under a set of selected equilibrium conditions, this apparatus can provide concentrations of bromoform in two phases: i.e., (1) gas phase (condensate)(2) liquid phase. The calculation of Henry's constant is as follows:

(6.2)

(a) **Definition of Henry's Constant**

$$C_B = H \cdot P_B$$

where

$C_B$  : Bromoform Concentration in the liquid phase (mol/L)

$P_B$  : Partial Pressure of Bromoform in the Gas phase (Pa)

Henry's constant is defined as  $H$  (mol/L)/(Pa) in the above equation.

(b) **Calculation of Henry's Constant**

i. Let the concentration in the liquid phase be  $C_B$ .

ii. Calculate the mole fraction of bromoform in the gas phase,  $Y_B$ , with the bromoform concentration of the condensed phase

iii. The partial pressure of bromoform in the gas phase,  $P_B$  is given by the following equation.

$$Y_B = P_B / \pi$$

Where  $\pi$  is the total pressure (= saturation pressure of water at the given temperature, the mole fraction of water being 1 approximately)

iv. Henry's constant is obtained by the following equation:

$$H = C_B / P_B$$

For water,  $Y_w = P_w / \pi$ ,  $Y_w \approx 1$ , then  $P_w \approx \pi = P_0$

When  $P_0$  is the vapor pressure of pure water.

### 2.3 Experimental Conditions

Following experimental conditions were used to obtain Henry's constant.

- (a) Seawater, (concentration Factor, C.F = 1.0)
- (b) Brine, (Concentration Factor, C.F. =1.4)
- (c) Temperature -- 40°C, 65°C, 90°C
- (d) Bromoform concentration -- 10 and 100 mg/L

### 3. Results

Before carrying out any experiment with vapor-liquid equilibrium apparatus, it is first leak tested. Typical data of leak test at 50 mm Hg is shown in Figure 2.

Data obtained with equilibrium apparatus and required for obtaining Henry's Constant is shown in Table No.2. It also shows the bromoform concentration in different sample viz. stock solution, Gas phase condensate, liquid-phase retained phase and traps to calculate the mass balance. Temperature and pressure at which experiments were carried out are given in Table 3. Calculated Henry's constants are also given in Table 3. Table 5 gives Bromoform concentration in gas phase condensate (Distillate).

### 4. Discussion

Vapor liquid equilibrium apparatus was leak tested at 50 mm Hg pressure. Plot of pressure as function of lapse time is shown in Fig. 2. It can be seen from the graph that the rate of leakage is quite low up to 90 minutes. Pressure remained at about 50 mm Hg. However, after 90 minutes of lapse, pressure started increasing slowly and reached value of about 70-72 mmHg at the end of 180 minutes. This leak rate after 120 minutes was not expected to interface with the experiments as the duration of each experiment was less than 90 min. Experimental conditions and bromoform concentrations in different samples from 15 runs are given in Table 2. Apart from stock solution concentration and volume of samples used, the table indicates the values of four more samples viz. gas phase sample which is condensed, liquid phase, retained phase, and trap (vent gas) samples. To see the mass balance, % recovery has been calculated and is indicated in the last column of Table 2. It can be seen that the recovery in general ranges between 70-105%. However, results from first two runs show only 10-12% recovery which is due to heavy leakage in the initial experiments. Variation in % recovery between 70-105% may be due to escape of some bromoform during sample collection. However, if care is taken at the time of sample collection i.e., during release of vacuum and sample drain, % recovery can be improved. One has to take care that no unnecessary bubbling take place during vacuum release.

Table No.3 indicated calculated Henry's constant obtained using data from Table No.2. A model calculation of Henry's constant of bromoform using raw data from Table No.2 is given in Table 4. A typical calculation for run No.14 using brine sample with concentration ratio = 1.4 at 80°C is shown in this table. One can see from Table No.3 that Henry's constant (H)

(6.2)

is temperature and pressure dependent. Plot of log H as function of temperature ( $^{\circ}\text{C}$ ) was found to be linear (Fig. 3). Relation between Henry's constant and temperature ( $T^{\circ}\text{C}$ ) can be mathematically expressed as

$$\log H = 1.0511 - 0.02458(T)$$

Where intercept = 1.0511 and slope = 0.0245 are obtained from Fig. 3 at  $T = 0$ . However, at temperature ( $T^{\circ}\text{C}$ ) = 30 the value of intercept is 0.24 and slope = 0.0245.

Fig. 3 show the log H vs temperature plot for both experimental and best fit values. It is obvious from the plot that as temperature increase Henry's constant decrease with negative slope.

It can be seen from Fig. 3 that Henry's constant is independent of feed water total dissolved solids; i.e., whether it is seawater (concentration factor 1.0) or brine (concentration factor 1.4). Further, it is also evident that Henry's constant is independent of concentration of bromoform in the test solutions, which were varied from 7.43 to 106 ppm. Table No.5 shows the amount of bromoform carried over to gas phase condensate. Amount detected in gas phase condensate as function of temperature is plotted and is shown in Fig. 4. It may be seen from Table 5 and Fig. 4 that % carry over of bromoform is in the range between 2 to 4% at equilibrium conditions and the carry over indicates an increasing trend with the temperature.

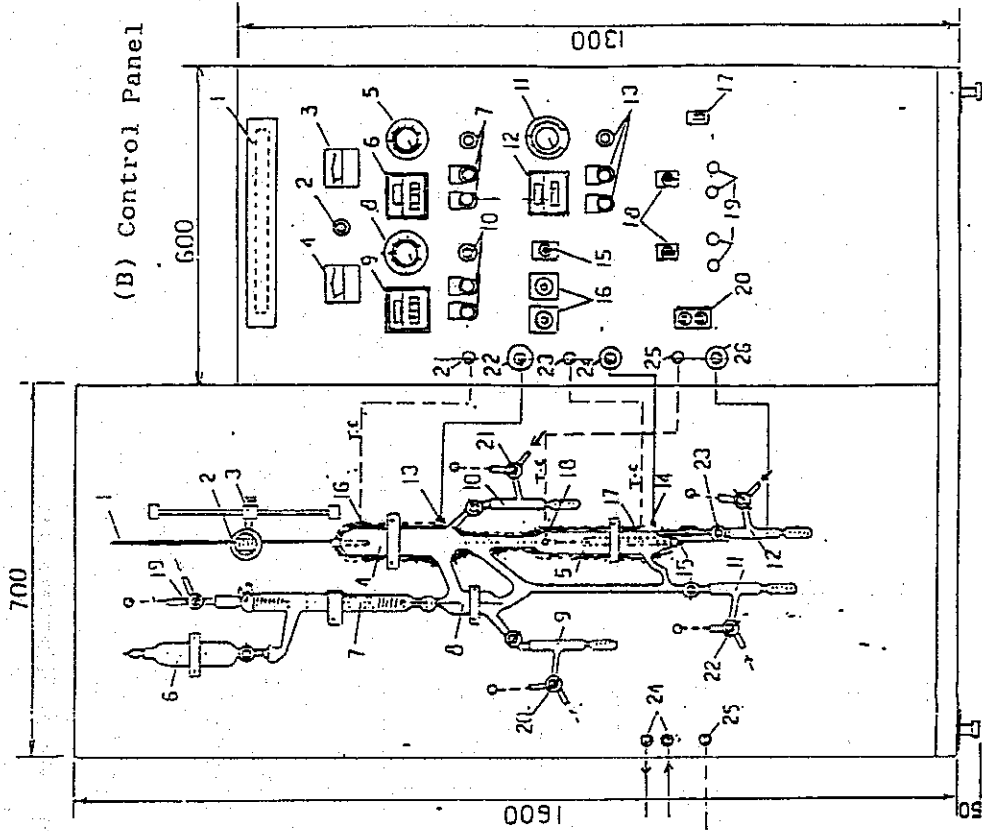
## 5. Conclusions:

Following are the conclusions of the experimental results obtained with bromoform:

- (i) Henry's constant (H) is temperature (T) dependent and varies inversely with temperature.
- (ii) Henry's constant is independent on bromoform concentrations in the test solutions.
- (iii) Mathematical relationship of H and T can be expressed as  
$$\log H = 1.0511 - 0.0245 (T)$$
- (iv) Seawater dissolved salts contents do not have any affects on Henry's constant values.

(6.2)

(A) Vapor/Liquid Equilibrium System



(C) Vacuum/Exhaust System

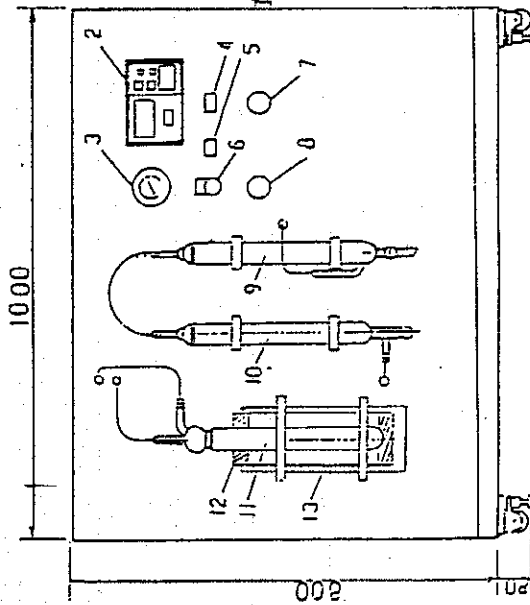


Fig. 1 Configuration of Vapor-liquid equilibrium apparatus

(6.2)

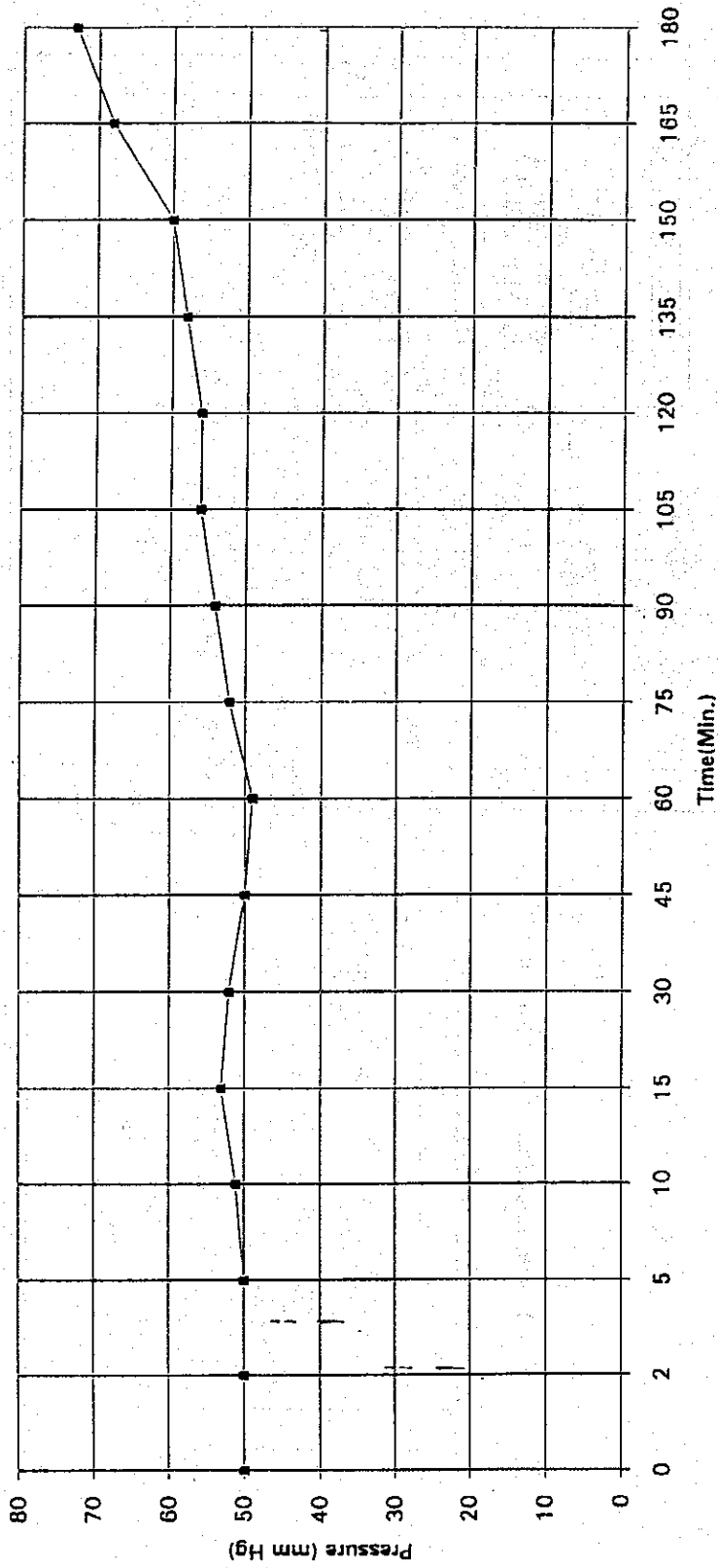


Fig. 2 Pressure vs. lapse time during leak test



(6.2)

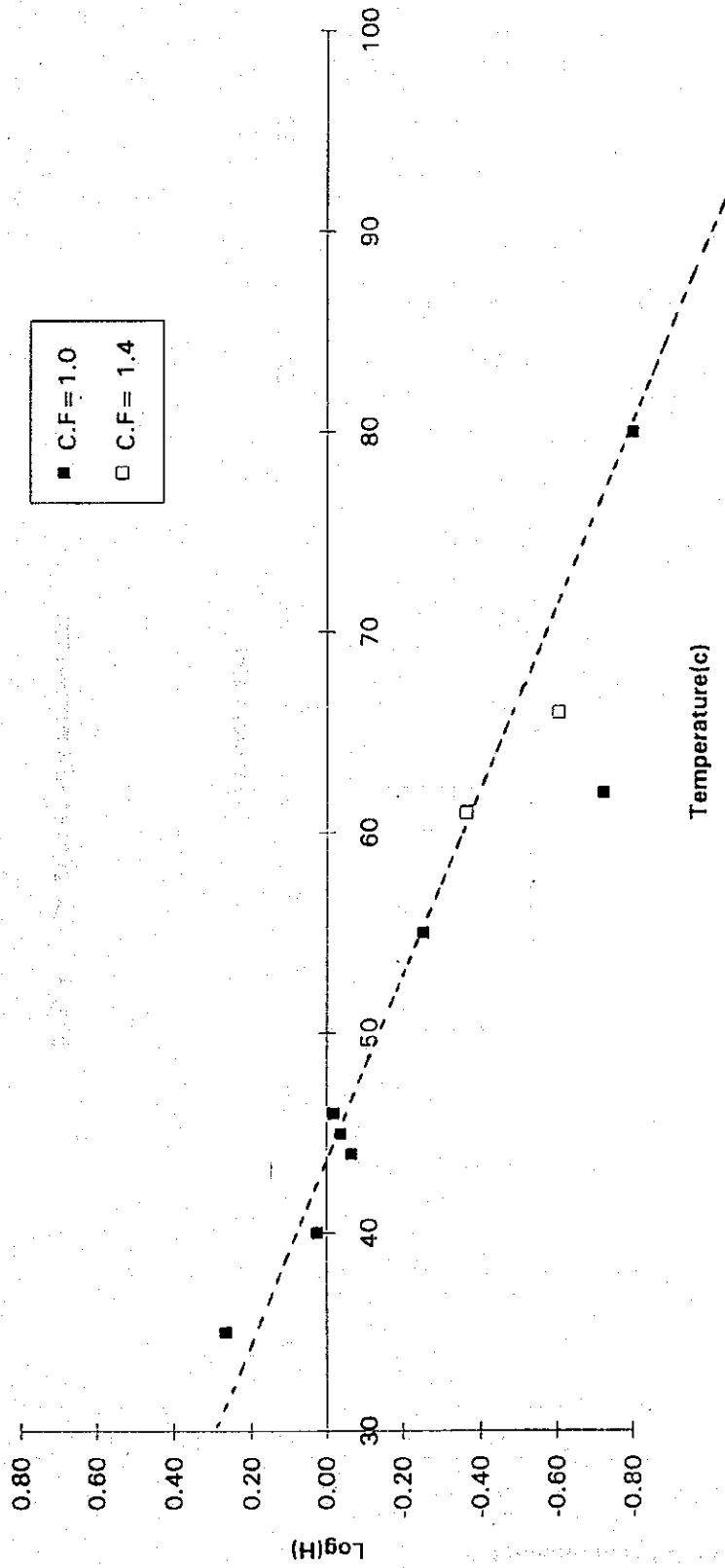


Fig. 3 Relationship between Henry's constant and temperature

(6.2)

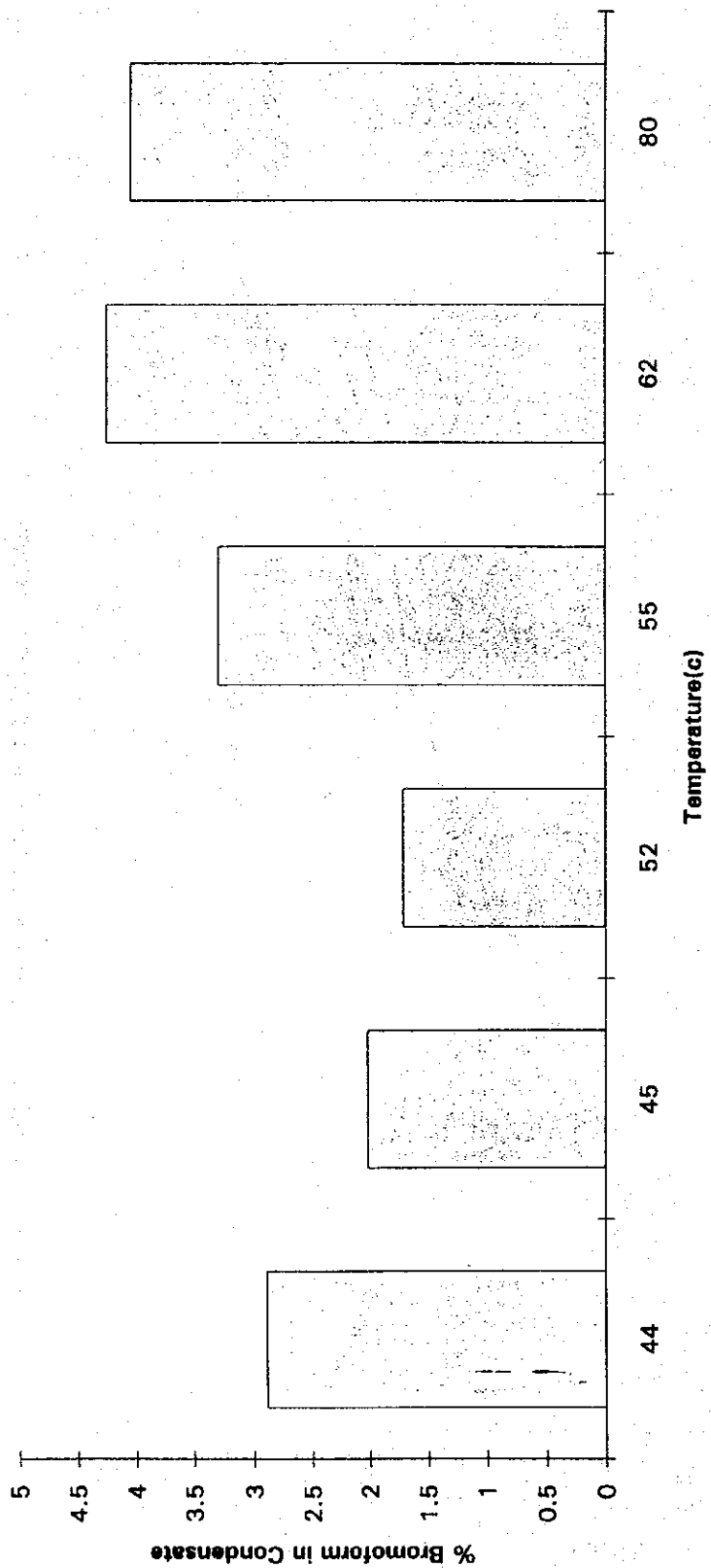


Fig. 4 Carryover of bromoform

(6.2)

**Table 1-1**

**Specification of the Vapor-liquid equilibrium (3/3) equipment for  
Vacuum/decompression discharge system**

S. No.	Name
1	Vacuum joint
2	Pirani pressure gauge
3	Borden pressure gauge
4	Vacuum control switch
5	Vacuum pump switch
6	Power switch
7	Leak valve
8	Streaming control valve
9	Air cleaning column
10	Air drying column
11	Gas gathering column
12	Aeration column
13	Vacuum vessel
14	Surge tank

(6.2)

**Table 1-2**

**Specification of the vapor-liquid equilibrium (2/3)  
instrumentation/operation/casing of adjustment**

S. No.	Name
1	Panel illumination lamp
2	Pilot lamp
3	Ampere meter for still heater
4	Voltmeter for still heater
5	No. 1 Heat volume controller
6	No. 1 Temp. controller
7	No. 1 Operation switch, pilot lamp
8	No. 2 Heater volume controller
9	No. 2 Temp. controller
10	No. 2 Operation switch, pilot lamp
11	No. 3 heat volume controller
12	No. 3 Temp. controller
13	No. 3 Operation switch, pilot lamp
14	Time (Unit - T)
15	Buzzer (Unit - T)
16	Circuit Breaker
17	Spare switch
18	Connector operated by switch - 18
19	Spare outlet
20	No. 1 Heater sensor
21	No. 1 Heater joint
22	No. 2 Heater sensor out
23	No. 2 Heater joint
24	No. 3 Still heater sensor out
25	No. 3 Still heater joint

(6.2)

**Table 1-3**

**Specification of the vapor-liquid equilibrium (1/3)  
body and frame**

S. No.	Name
1	Thermometer
2	Lens for reading thermometer
3	Lens positioning parts
4	Equilibrium equipment, upper
5	Equilibrium equipment, still unit
6	sample supply column
7	Vapor condensing column
8	Liquid distributing unit
9	No. 1 Sample gathering Unit
10	No. 2 Sample gathering Unit
11	No. 3 Sample gathering Unit
12	No. 4 Sample gathering Unit
13	No. 1 Heater & Cord
14	No. 2 Heater & Cord
15	No. 3 Still heater & cord
16	No. 1 Heater & Thermo sensor
17	No. 2 Heater & Thermo sensor
18	No. 3 Still heater & thermo sensor
19	Changeover cock, vacuum/ambient
20	No. 1 Changeover cock, vacuum/ambient
21	No. 2 Changeover cock, vacuum/ambient
22	No. 3 Changeover cock, vacuum/ambient
23	No. 4 Changeover cock, vacuum/ambient
24	Cold water supply, in out
25	Vacuum pump joint

Table 2 Data obtained by Vapor-liquid equilibrium apparatus

Run No	Date	Temp [C]	Conc. Factor	Stock		Distillate		Liquid Phase		Retained		Trap		% Recovery
				Conc. (ppm)	Vol. (ml)	Conc. (ppm)	Vol. (ml)	Conc. (ppm)	Vol. (ml)	Conc. (ppm)	Vol. (ml)	Conc. (ppm)	Vol. (ml)	
1	22-Oct-94	48	1.0	15.5	275	4.69	5.5	0.77	45	0.65	235	1.16	200	10.47
2	25-Oct-94	57	1.0	10.7	275	3.35	5.5	0.363	45	0.63	235	0.89	200	12.24
3	26-Oct-94	55	1.0	8.26	275	15.43	6	5.198	48	2.81	220	2.8	200	88.97
4	29-Oct-94	48	1.0	7.92	275	6.378	5.5	17.88	38	3.24	230	0.59	200	72.4
5	29-Oct-94	44	1.0	7.92	275	8.99	7	9.7	33	4.98	225	0.42	200	72.8
6	30-Oct-94	52	1.0	10.5	275	6.952	7	13.74	46	9.25	220	0.43	200	97.38
7	30-Oct-94	55	1.0	9.65	275	12.42	7	12.33	48	2.49	220	0.38	200	49.03
8	1-Nov-94	45	1.0	9.62	275	14.02	7.5	16.32	47	3.47	220	1.7	200	74.69
9	5-Nov-94	35	1.0	107	275	110.7	8	158.6	48	20.1	230	0.78	200	44.98
10	6-Nov-94	46	1.0	103	275	243.9	8	322.7	44	25.2	225	4.65	200	80.08
11	7-Nov-94	40	1.0	102	275	80.71	7	84.69	48	48.8	230	2.44	200	58.16
12	8-Nov-94	80	1.0	106	275	146.2	8	149.2	50	25.4	225	1.85	200	50.38
13	9-Nov-94	62	1.0	105	275	166.2	8	106.3	50	25.2	225	6.5	200	47.02
14	21-Nov-94	61	1.4	7.43	275	12.98	8	15.32	48	3.54	205	3.29	200	108.7
15	27-Nov-94	66	1.4	7.44	275	14.98	7.5	12.55	48	2.11	220	0.44	200	61.96

(6.2)

**Table 3** Calculated Henry's constants

S. No	Run No.	Temperature		Pressure mmg Hg	Henry's Constant	Concentration Factor	Bromoform concentration ppm
		°C	°K				
1	9	35	308	43	1.85	1	7.92
2	11	40	313	55	1.060	1	102
3	5	44	317	70	0.859	1	7.92
4	8	45	318	70	0.923	1	9.62
5	10	46	319	72	0.962	1	103
6	6	52	325	97	1.1	1	10.46
7	7	54.8	327.8	98	0.56	1	9.65
8	13	62	335	187	0.19	1	105.2
9	12	80	353	355	0.16	1	108
10	14	61	334	149	0.434	1.4	7.432
11	15	66	339	187	0.24	1.4	7.437

(6.2)

**Table 4** Calculated Henry's constants of bromoform

$$H = (C_L/M)/P \quad \text{mol}/(\text{L mmHg})$$

$$P = (MF_g \cdot P_{\text{steam}}) \quad \text{mmHg}$$

$$MF_g = (C_g/M) / \{(C_g/M + 1000/18)\} -$$

$$M = 252.73, P_{\text{steam}} : \text{Steam table}$$

Items	Symbol	Unit	Calculated values	Note
1. Run No.			14	
2. Date measured			21/11/94	
3. Steam Temperature	$T_w$	$^{\circ}\text{C}$	61	
4. Conc. Stocked	$C_s$	mg/L	7.432	
5. Concentration measured Liquid phase	$C_l$	mg/L	15.322	
6. Gas phase	$C_g$	mg/L	12.982	
7. Mole concentration of $\text{CHBr}_3$ in liquid phase	$C_l/M$	mol/L	$0.0606 \times 10^{-3}$	5) /252.72
8. of $\text{CHBr}_3$ in gas phase	$C_g/M$	mol/L	$0.05136 \times 10^{-3}$	6) /252.72
9. of 1L of $\text{H}_2\text{O}$ in gas phase	55.56	mol/L	55.56	
10. of $\text{CHBr}_3 + \text{H}_2\text{O}$ in gas phase		mol/L	55.560513	8) + 9)
11. Mole fraction in gas phase	$MF_g$	-	$0.00093 \times 10^{-3}$	8) /10)
12. Partial pressure of steam	$P_{\text{steam}}$	mmHg	149	
13. of $\text{CHBr}_3$ gas	$P$	mmHg	$0.13936 \times 10^{-3}$	11) * 12)
13. Henry's constant	$H$	mol/ (L mmHg)	0.434	7) /13



(6.2)

**Table 5 Bromoform concentration in gas phase condensate**

Temp. (C)	Feed Conc. (Micrograms)	Distillate. Conc (micrograms)	% in Condensate
44	2.178	0.0629	2.8879706
45	28.05	0.565	2.0142602
52	2.877	0.049	1.703163
55	2.648	0.087	3.2854985
62	28.93	1.229	4.24181853
80	29.7	1.2	4.040404

