

Fig. 3.1.1 Relationship between Amount of 1N Na₂CO₃ Solution Added and M-Alkalinity of Brine obtained by this Experiment

$$\text{Assumed alkalinity after having added 1N Na}_2\text{CO}_3 \\ = (50)(10^3) V_{NA}/V_s + \text{ALKs [ppm as CaCO}_3] \dots\dots\dots 3.1.1$$

where

(50)(10³): Alkalinity of 1N Na₂CO₃ solution

V_{NA}: Amount of 1N Na₂CO₃ solution added [lit.]

V_s: Amount of brine to be added [lit.]

ALKs: Alkalinity of brine before being added [ppm as CaCO₃]

Since V_{NA}=0.01, V_s=0.5 and ALKs=181.7 in a normal case, the assumed alkalinity is 1,181.7 ppm as CaCO₃ and the value that the M-alkalinity of filtrate after having separated precipitation has been deducted from the assumed alkalinity becomes precipitation weight converted to CaCO₃.

3.2 Experimental Condition

Though the experimental condition has been established in accordance with the initial plan, it has partly been modified in order to adapt it to actual operating and environmental conditions as much as possible. Variable factors are shown below.

A. Brine temperature

Since the outlet temperature of the brine heater during normal operation is 90.56 °C in Al Jubail Phase-II plant, it has been decided to conduct the experiment at 95°C, 80°C and 50°C.

B. Brine concentration

It has been determined to be in accordance with the operating condition in Al Jubail Phase-2 plant.

C. Concentration of scale inhibitor to be added

It has been determined by using the standard concentration of 5 ppm of polymeric carboxylic acid base scale inhibitors as a yardstick.

However two different concentration namely 3ppm and 10ppm were considered for comparison.

D. Concentration of Oil to be added

Three conditions in the range of 1-100x10⁻³ ml/l have been adopted.

E. Retention time of scale inhibitor

Three conditions, i.e. 5 minutes, 17 minutes and 60 minutes have been adopted.

Table 3.2.1 shows the combination of these variable factors which allows us to gain the most effective results.

Table 3.2.1 Experiments Condition

TEST NUMBER	TEMPERATURE	RETENTION TIME	CONCENTRATION OF SCALE INHIBIT. *)	CONCENTRATION OF OIL	NOTE
	°C	min	ppm	ppm	
S1b1	95	60	0	0	
S101	95	60	5	0	
S102	95	60	5	1	
S104	95	60	5	100	
S105	95	60	10	100	
S1b4	95	17	0	0	
S109	95	17	5	0	
S110	95	17	5	1	
S111	95	17	5	100	
S1b2	95	5	0	0	
S1b3	95	5	0	100	
S112	95	5	3	100	
S106	95	5	5	0	
S107	95	5	5	1	
S108	95	5	5	100	
S113	95	5	10	100	
S2b1	80	60	0	0	
S201	80	60	5	0	
S202	80	60	5	1	
S203	80	60	5	10	
S204	80	60	5	100	
S205	80	60	3	0	
S206	80	5	5	0	
S207	80	5	5	1	
S208	80	5	5	100	
S3b1	50	60	0	0	
S301	50	60	5	0	
S302	50	60	5	1	
S304	50	60	5	100	

*) : SCALE INHIBIT. represents the scale inhibitor using in this tests.

3.3 Experimental Method

Experiments can roughly be classified to the following two items.

- A. Preparation of concentrated seawater
- B. Experiment on the deposition of precipitation

3.3.1 Preparation of Concentrated Sea Water (Brine)

(1) Experimental Equipment

To imitate recirculating brine of actual plants which have adopted the C.D. Method as a method of preventing scaling, vacuum evaporation must be adopted under the temperature of 60°C and below to concentrate seawater to 1.4 times without causing precipitation. For this reason, a rotary evaporator on the market has been used. It takes about one hour for the preparation of one batch 350 ml with this rotary evaporator. Fig. 3.3.1 shows the configuration of the rotary evaporator adopted.

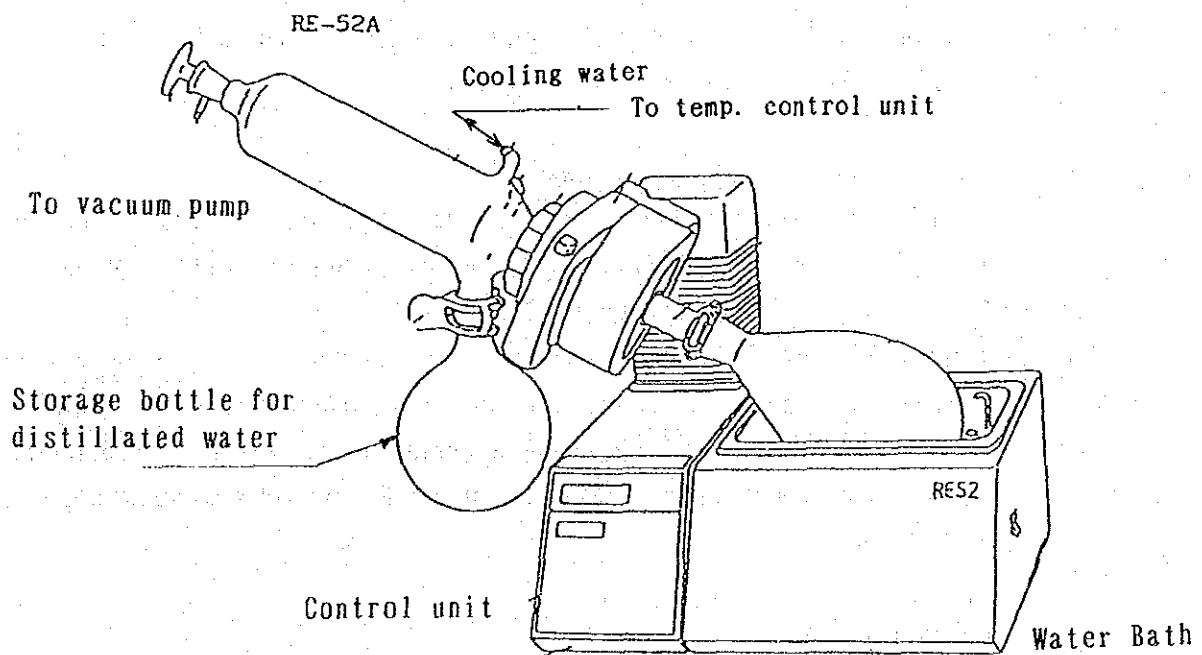


Fig.3.3.1 Configuration of Rotary Evaporator using for Concentration of Seawater

(2) Experimental Method

Brine has been prepared according to the following procedures.

* Sampling of raw seawater:

Raw seawater has been sampled at the inlet of feed seawater to the deaerator of Al Jubail Phase-II MSF Plant No. 31 Machine. (Only chlorination has been done.)

* Filtration of seawater:

Seawater has been filtered with filter paper to remove suspended substances which have possibility to become kernels at the time of precipitation. The method of filtration under reduced pressure has been adopted, since seawater of about 20 liters must be treated at a time.

* Preparation of brine:

Seawater has been concentrated to 1.4 times at 60°C with the rotary evaporator. No occurrence of precipitation has been confirmed at this time.

* Keeping of brine

Brine of 20 to 50 liters has been kept in a polyethylene vessel. Water quality has been analyzed and finely adjusted by adding pure water at this time.

(3) Chemical Constituent of Raw Seawater and Brine

Raw seawater has been concentrated twice under reduced pressure to prepare brine and the concentration rate of brine has been finely adjusted to 1.4 by adding pure water. The chemical constituent of raw seawater and brine is shown in Table 3.3.1.

The first concentration work has been done on the basis of chlorine ion. However, when the second concentration work has been done, concentration in M-alkalinity has been adjusted to 1.4 times by reducing the speed of concentration using a pressure reducing pump and suppressing the diffusion of CO₂, since concentration in M-alkalinity could not reach the expected rate at the first concentration work.

(4) Analytical Apparatus and Method

- | | |
|--------------------------|-------------------------------|
| * pH: | pH meter |
| * Electric Conductivity: | Electrical conductivity meter |
| * M-alkalinity: | Automatic titrater |
| * Chloride ion: | Wet analysis |
| * Calcium ion: | ICP emission spectrometer |

* Magnesium ion: ICP emission spectrometer

* Concentration Factor: Salt meter

Table 3.3.1 Chemical Constituent of Raw Seawater and Brine

I T E M	Raw Seawater	Brine			
		# 1	CF	# 2	CF
pH (25 °C)	8.17				
E. Conductivity (μ S/cm)		77,246			
M-Alkalinity (ppm as CaCO ₃)	128.8	154.1	1.20	181.7	1.41
Chlorine ion (ppm)	23,513	33,240	1.41	31,769	1.36
Calcium ion (ppm)	400	630	1.57		
Magnesium ion (ppm)	1,400	1,967	1.40		

note CF:Concentration Factor

3.3.2 Experiment on the Deposition of precipitation

(1) Experimental Equipment

In order to observe the experimental conditions shown in Table 3.2.1, the three-neck flask attached to the cooler has been used and condensed water has totally been returned to this flask, as shown in Fig. 3.3.2. An oil bath and a vacuum pump have been used for raising temperature and keeping it constant.

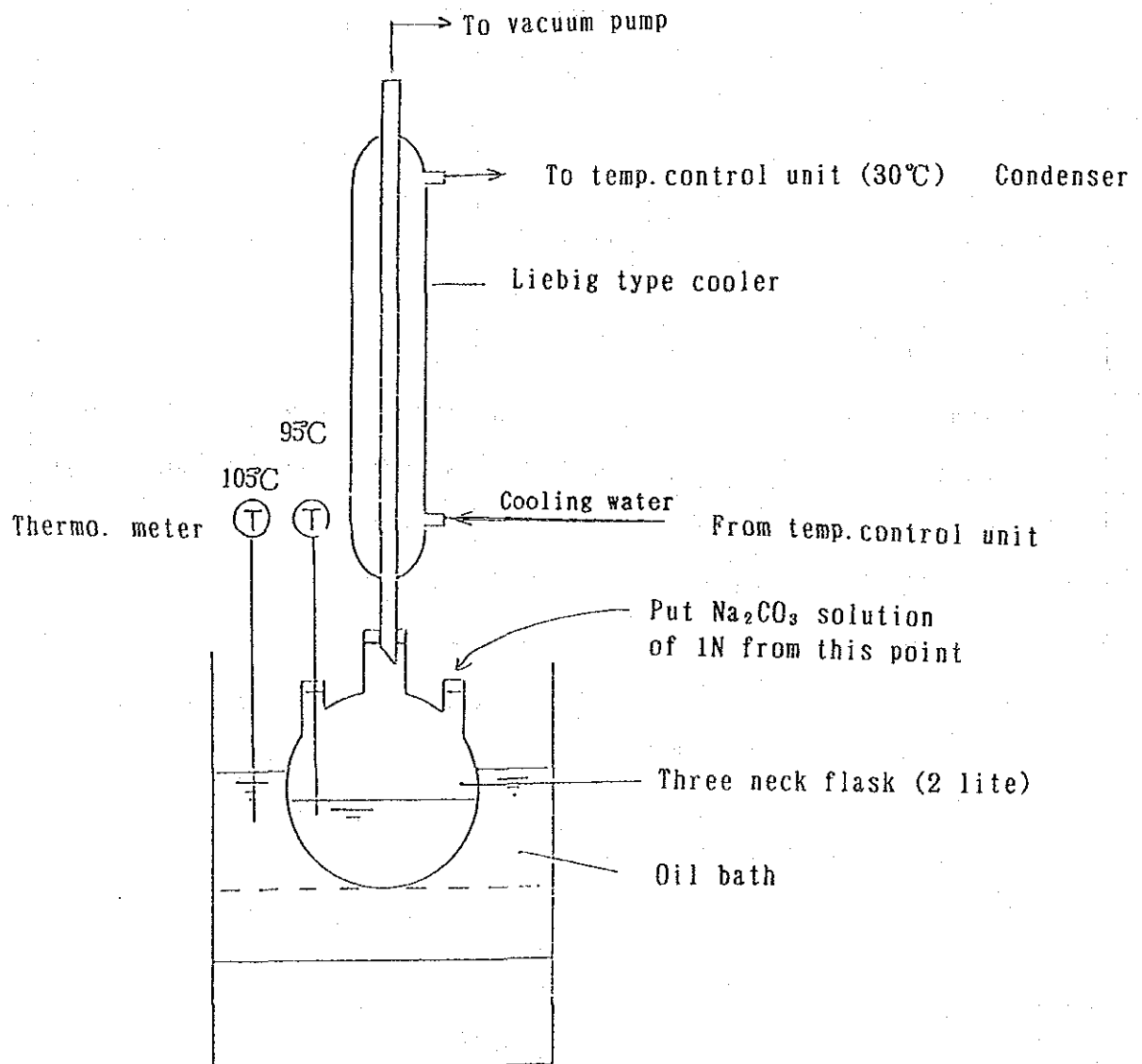


Fig.3.3.2 Equipment Apparatus using for Deposition of Precipitation

(2) Experimental Method

Experiments on the deposition of precipitation have been conducted according to the following procedures.

1) In case both oil and a scale inhibitor are added

* Charging of brine

Specified quantities of oil and a scale inhibitor were added to 500ml of the concentrated-brine and stirred with a blender for 20 seconds. The prepared brine is charged immediately into a three-neck flask attached to the cooler.

A sample of brine into which oil of 100 ppm was added and has been stirred with a blender for 20 seconds, the particle sizes of emulsified oil have been measured with microscope. Almost all particles of emulsified oil were $10\ \mu\text{m}$ or smaller and dispersed uniformly as shown in Fig. 3.3.3.

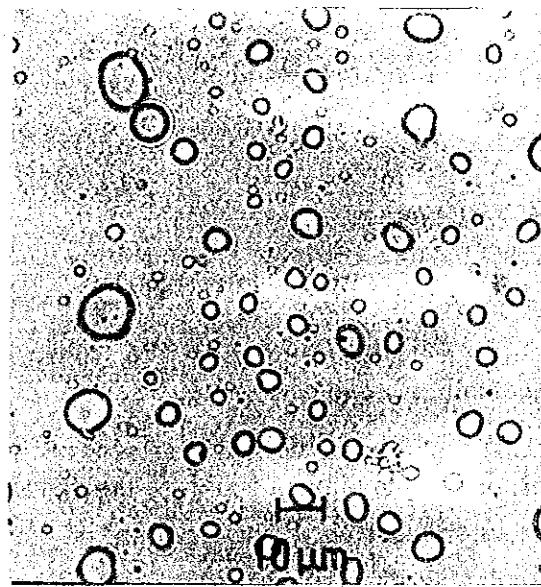


Fig.3.3.3 Microscope Photo for Measurement of Oil Particle Size after Mixing Brine with Oil by Blender

* Heating of brine:

To keep specified temperature for 30 minutes while returning back condensed water. To confirm no occurrence of precipitation.

* Time of beginning of reaction and breakage of supersaturated state:

To add 1N Na_2CO_3 of 10 ml to brine in this state and to stir quickly. This time is decided to be the time of the beginning of reaction. When starting to add 1N Na_2CO_3 , M-alkalinity begins to decrease with the formation of precipitation. When adding 1N Na_2CO_3 further, there is a point where M-alkalinity begins to increase. This point is the breaking point of a supersaturated state.

* Formation of precipitation:

When adding 1N Na_2CO_3 further, precipitation increases together with increase in M-alkalinity.

To add 1N Na_2CO_3 of 10 ml calculated by Equation 3.1.1 to increase M-alkalinity up to 1000 ppm as CaCO_3 .

* Separation of precipitation:

To form precipitation for specified period of time, and then to quickly filtrate precipitation with No. 5C filter paper.

* Treatment of precipitation and filtrate:

Supposing the necessity of mass balance check and for observing the shapes of crystals of precipitation, to keep both precipitation and filtrate.

2) In case oil is not added and a scale inhibitor is added.

* Charging of brine

To add specified quantity of a scale inhibitor to 500ml of the concentrated brine and to stir then to charge it into the three-neck flask attached to the cooler.

To charge this flask with it right after then. (Hereinafter, same as 1)

3) In case both oil and a scale inhibitor are not added

* Charging of brine:

To charge the three-neck flask that is attached to the cooler with 500ml of concentrated brine. (Hereinafter same as 1)

(3) Name, Physical Properties and Composition of Oil Added

- * Name: Light Diesel Oil
- * Physical properties: Specific gravity: 0.8679 (15/4°C),
- * Viscosity: 2.848 cSt,
- * Sulfur: 0.64
- * Method of analysis: Gas chromatography analysis
- * Type of analyzer
 Carbon number 12 or below: SIMADZU GC-14A
 Carbon number 13 or above: SIMADZU GC-7A
- * Constituent: Table 3.3.2 shows the rates of contents of organic substances included in this oil by carbon number.

Table 3.3.2 Concentration of Hydrocarbon contained in Light Diesel Oil

C _N	Conc. (ppm)	C _N	Conc. (ppm)	C _N	Conc. (ppm)
C-1	ND	C-11	9,380	C-20	8,700
C-2		C-12	13.2*10 ³	C-21	3,400
C-4		C-13	12.6*10 ³	C-22	1,850
C-5	11	C-14	24.9*10 ³	C-23	708
C-6	128	C-15	27.6*10 ³	C-24	458
C-7	416	C-16	18.5*10 ³	C-25	190
C-8	647	C-17	28.3*10 ³	C-26	130
C-9	3,080	C-18	21.5*10 ³	C-27	86
C-10	9,620	C-19	12.3*10 ³	C-28	11

C_N:
Carbon No.

Figs. 3.3.4 and 3.3.5 shows data for C_{12} or below and C_{13} or above among measured data to calculate the rates of contents by carbon number mentioned above respectively.

(4) Name, Physical Properties and Composition of Scale Inhibitor

- * Name: Scale inhibitor "x"
- * Specific gravity: 1.22
- * pH: 1.0-2.0
- * Appearance: Amber Liquid
- * Major Constituent: Polymeric carboxylic acid

(5) Apparatus and Methods

- * SEM Photo: Scanning electron microscope Hitachi S-800
- * Others: Hereinafter, same as 3.3.1 (4)

4. Results and Discussion

4.1 Experimental Results

Experimental on the deposition of precipitation has been made on the basis of experimental conditions shown in Table 3.2.1.

Table 4.1.1 shows measured results on the M-alkalinity of each filtrate.

Since the tendency that particles of precipitation become fine has been observed during this experiment when temperature becomes 80°C or above and oil concentration becomes 100 ppm, precipitation shown in Table 4.1.2 have been observed by SEM examination. Figs. 4.1.1 to 4.1.8 show the results.

4.2 Discussion

4.2.1 Method of Evaluating the Action of Scale Inhibitors

The aim of this research is to examine and compare the performance of scale inhibitors in use now in the case where oil intrudes into water by carrying out laboratory-scale experiments. Authors therefore wish to review the methods of evaluating the effect of the scale inhibitor used in this experiment first.

As stated in Chapter 2, scale inhibitors have two effects, i.e. A) threshold effect and B) crystal distortion effect.

In the case where the threshold effect comes into force, the M-alkalinity to be detected which concerns CaCO_3 precipitation becomes more than the critical concentration of CaCO_3

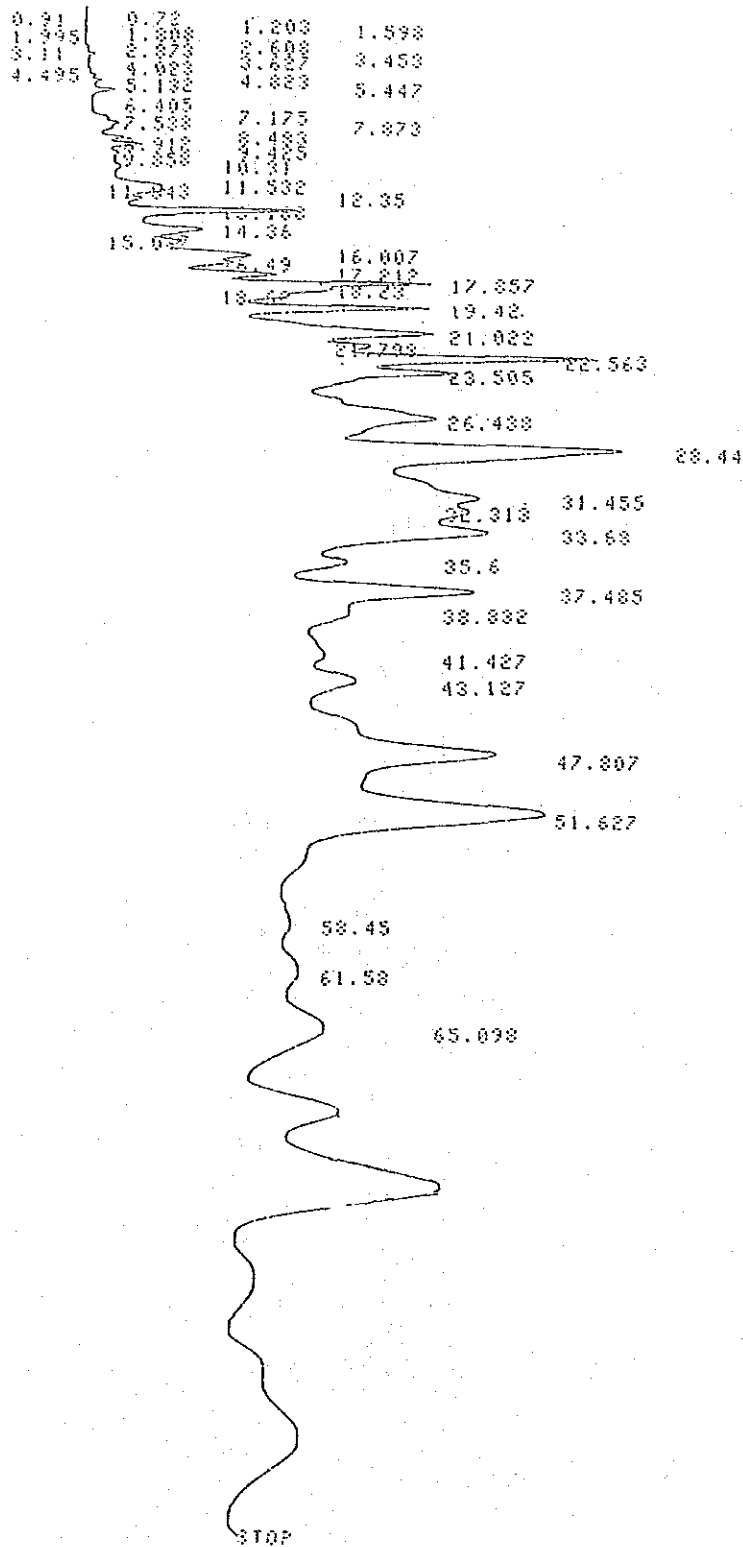


Fig. 3.3.4-1 Gas-Chromatogram of Light Diesel Oil added for this Experiment (Carbon Number: up to 12)

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.808	2000			0.0058	
2	2.608	6318			0.0177	C-05
3	2.873	4227			0.0118	
4	3.11	15140			0.0424	C-06
5	4.023	6577			0.0184	
6	4.495	12171			0.0341	
7	4.823	19194			0.0538	
8	5.132	2332			0.0065	
9	5.447	58644			0.1643	C-07
10	6.405	7430			0.0208	
11	7.175	5549			0.0155	
12	7.538	25638			0.072	
13	7.873	11354			0.0318	
14	8.483	41377			0.1159	
15	8.912	82519			0.2312	C-08
16	9.425	24100			0.0675	
17	9.858	3194			0.009	
18	10.31	31906			0.0894	
19	11.532	147411			0.413	
20	11.843	129955	V		0.3641	
21	12.35	33383			0.0935	
22	13.168	583695			1.6355	C-09
23	14.36	249071			0.6979	
24	15.087	67230			0.1884	
25	16.007	408506			1.1222	
26	16.49	184973	V		0.5183	
27	17.212	309380			0.8669	
28	17.857	841531	V		2.358	
29	18.23	341340	V		0.9564	
30	18.62	163377	V		0.4572	C-10
31	19.42	685493			1.9208	
32	21.022	1380078			3.867	
33	21.798	580900	V		1.6277	
34	22.563	1797889	V		5.0377	C-11
35	23.505	1191699	V		3.3392	
36	26.438	1393062			3.9034	
37	28.44	2507002			7.0246	C-12
38	31.455	705274			1.9762	
39	32.313	315480	V		0.884	
40	33.68	318180			2.2923	
41	35.6	287066			0.8044	
42	37.485	1390775			3.897	
43	38.832	113172			0.3311	C-13
44	41.427	193494			0.5422	
45	43.127	528707			1.4814	
46	47.807	2649522			7.4242	
47	51.627	3597298			10.0797	C-14
48	58.45	214783			0.6018	
49	61.58	302389			0.8473	
50	65.098	1421771			3.9838	
51	70.46	1292753			3.6223	
52	75.205	5269773			14.766	C-15
53	80.91	843376			2.3631	
54	86.823	213908			0.5994	
55	90.995	2178269			5.1035	
	TOTAL	35688656			100	

Fig. 3.3.4-2 Estimation of Carbon Number from Gas-Chromatogram

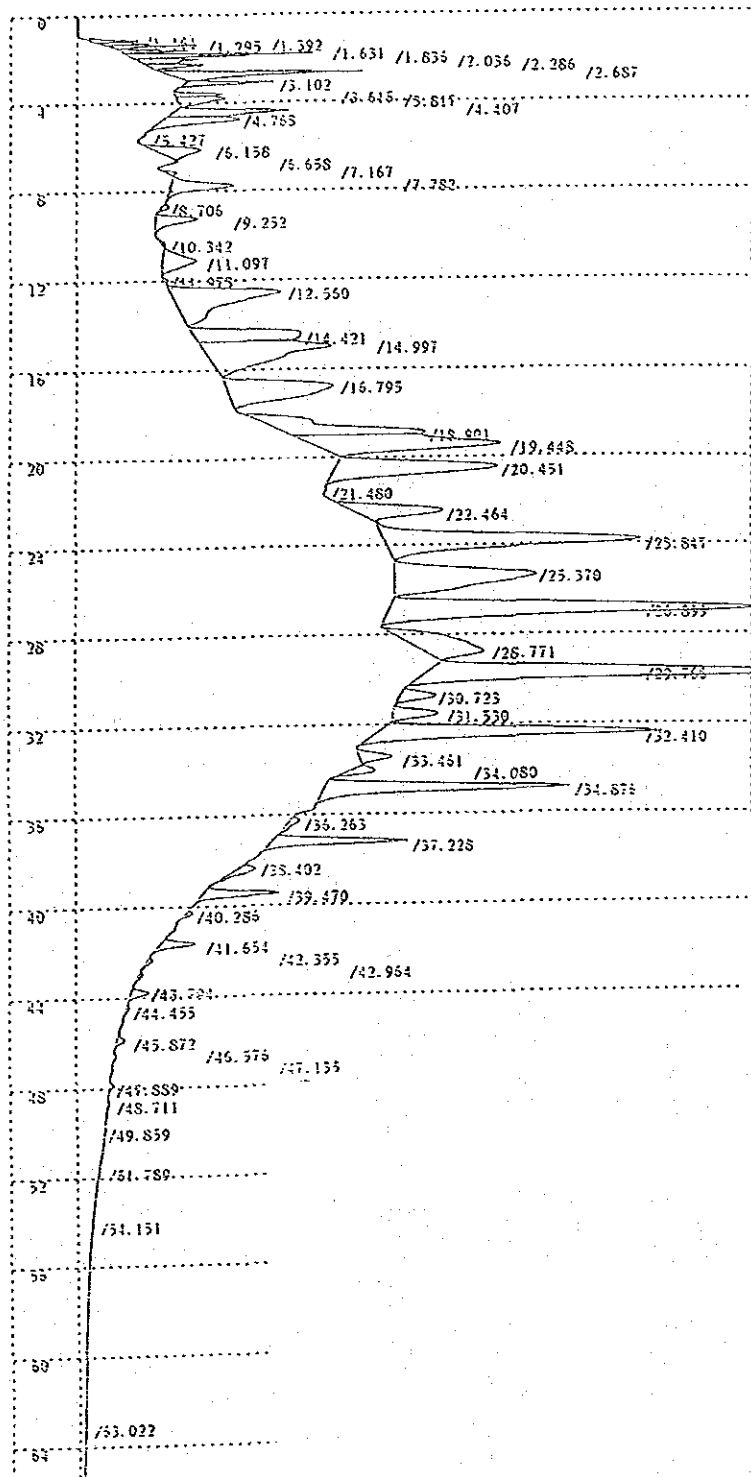


Fig. 3.3.5-1 Gas-Chromatogram of Light Diesel Oil added for this Experiment (Carbon Number: more than 13)

CH	PKNO	TIME	AREA	HEIGHT	MK
1	2	1.161	120888	18043	
	3	1.295	102592	18195	V
	4	1.392	169544	33515	V
	5	1.631	155451	25256	
	6	1.836	450195	69589	
	7	2.036	224317	23179	V
	8	2.286	196310	20956	V
	9	2.687	856388	73273	
	10	3.102	263311	32690	
	11	3.615	167460	18000	
	12	3.817	321303	18332	V
	13	4.407	654600	43231	
	14	4.768	581295	29030	V
	15	5.427	10025	995	
	16	6.158	405350	16394	
	17	6.658	25815	1786	
	18	7.167	37455	3115	
	19	7.782	549204	23931	
C-12	20	8.706	41425	2732	
	21	9.252	336767	15830	
	22	10.342	17470	1019	
	23	11.097	456619	12837	
	24	11.973	16013	1342	
C-13	25	12.56	1918664	41050	
	26	14.421	1266421	40452	
	27	14.997	2322311	48874	V
C-14	28	16.795	1972882	40202	
	29	18.901	1706937	52561	
	30	19.448	2641127	71027	V
C-15	31	20.451	2317603	61455	
	32	21.48	11351	1058	
	33	22.464	1036011	34083	
C-16	34	23.847	3611472	96449	
	35	25.37	2724592	53006	
C-17	36	26.899	4700377	139496	
	37	28.771	1432288	22258	
C-18	38	29.766	4438173	150187	
	39	30.723	317430	13837	
	40	31.53	404091	17076	
C-19	41	32.41	2840897	107747	
	42	33.461	267674	12351	
	43	34.08	198783	9857	
C-20	44	34.876	2125784	91946	
	45	36.263	104802	3759	
C-21	46	37.228	921103	52074	
	47	38.402	168122	6608	
C-22	48	39.47	462224	28759	
	49	40.286	34469	2224	
C-23	50	41.654	212497	12935	
	51	42.355	29830	1661	
	52	42.964	25637	1229	
C-24	53	43.794	113509	6750	
	54	44.455	18145	1001	
C-25	55	45.872	55662	3070	
	56	46.576	20825	1160	
	57	47.135	9230	430	
C-26	58	47.889	22161	1439	
	59	48.711	24274	802	
C-27	60	49.859	10110	706	
C-28	61	51.789	5145	363	
	62	54.151	4986	247	
	63	63.022	5502	148	
TOTAL			46660848	1733604	

Fig. 3.3.5-2 Estimation of Carbon Number from Gas-Chromatogram

Table 4.1.1 Result of M-Alkalinity Measurement in Each Experimental Condition

TEST NUMBER	TEMP °C	RETEN- TION TIME min	CONC. OF S. INHIBIT. *) ppm	CONC. OF OIL ppm	CONCENTRATION **)		
					ALK _S	ALK _{FM}	ALK _F
					ppm as CaCO ₃		
S1b1	95	60	0	0	154.1	112.7	140.3
S101	95	60	5	0	154.1	98.9	126.5
S102	95	60	5	1	154.1	108.1	135.7
S104	95	60	5	100	154.1	94.3	121.9
S105	95	60	10	100	154.1	140.0	167.6
S1b4	95	17	0	0	181.7	131.1	131.1
S109	95	17	5	0	181.7	218.5	218.5
S110	95	17	5	1	181.7	174.8	174.8
S111	95	17	5	100	181.7	186.3	186.3
S1b2	95	5	0	0	181.7	455.4	455.4
S1b3	95	5	0	100	181.7	179.4	179.4
S112	95	5	3	100	181.7	216.2	216.2
S106	95	5	5	0	154.1	515.0	542.6
S107	95	5	5	1	181.7	388.7	388.7
S108	95	5	5	100	181.7	213.9	213.9
S113	95	5	10	100	181.7	216.2	216.2
S2b1	80	60	0	0	154.1	108.1	135.7
S201	80	60	5	0	154.1	210.5	238.1
S202	80	60	5	1	154.1	141.5	169.1
S203	80	60	5	10	154.1	138.0	165.6
S204	80	60	5	100	154.1	202.4	230.0
S205	80	60	3	0	154.1	89.9	117.5
S206	80	5	5	0	181.7	246.1	246.1
S207	80	5	5	1	181.7	262.2	262.2
S208	80	5	5	100	181.7	466.2	466.2
S3b1	50	60	0	0	154.1	197.8	225.4
S301	50	60	5	0	154.1	218.5	246.1
S302	50	60	5	1	154.1	207.0	234.6
S304	50	60	5	100	154.1	174.8	199.4

*) S. INHIBIT. :Scale inhibitor using in this tests

ALK_S:M-Alkalinity before heating, ALK_{FM}:M-Alkalinity of filtrate

ALK_F:M-Alkalinity be corrected of filtrate

Table 4.1.2 Precipitate for SEM Examination

TEST NUMBER	TEMPERATURE	RETENTION TIME	CONCENTRATION OF SCALE INHIBITOR	CONCENTRATION OF OIL
	°C	min	ppm	ppm
S1b2	95	5	0	0
S106	95	5	5	0
S108	95	5	5	100
S111	95	17	5	100
S1b1	95	60	0	0
S101	95	60	5	0
S104	95	60	5	100
S204	80	60	5	100

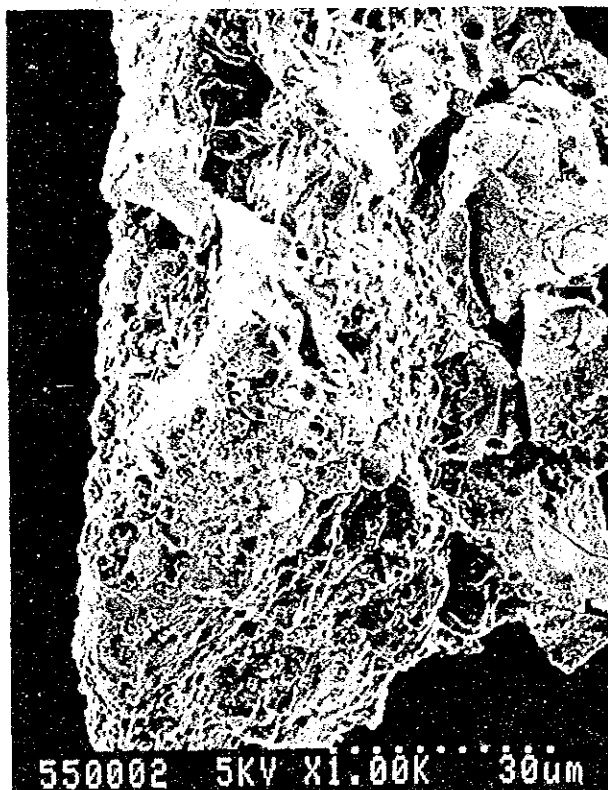
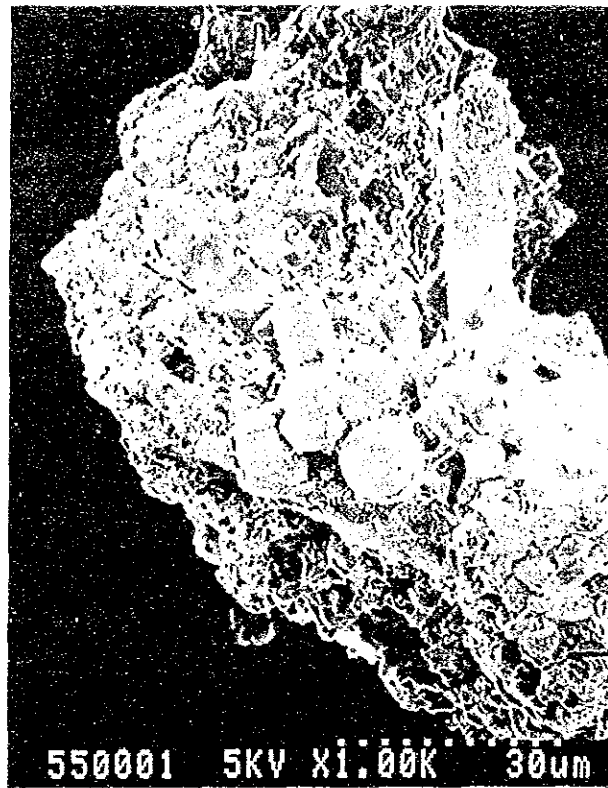


Fig.4.1.1 Result of SEM Examination of Scale Constituent Precipitated(Temp. 95°C, Retention Time 0 min., Scale Inhibitor Concentration 0ppm, Oil Concentration 9ppm)

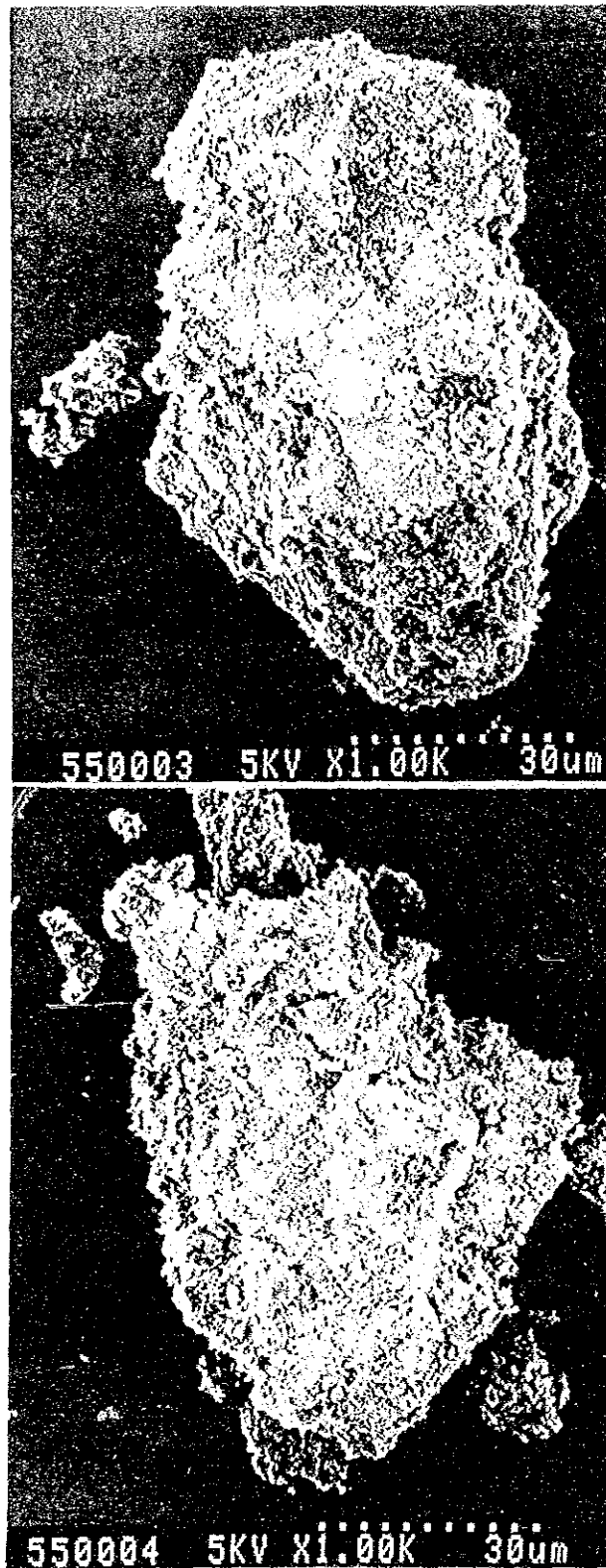


Fig.4.1.2 Result of SEM Examination of Scale Constituent Precipitated(Temp. 95°C, Retention Time 5 min., Scale Inhibitor Concentration 5ppm, Oil Concentration 0ppm)

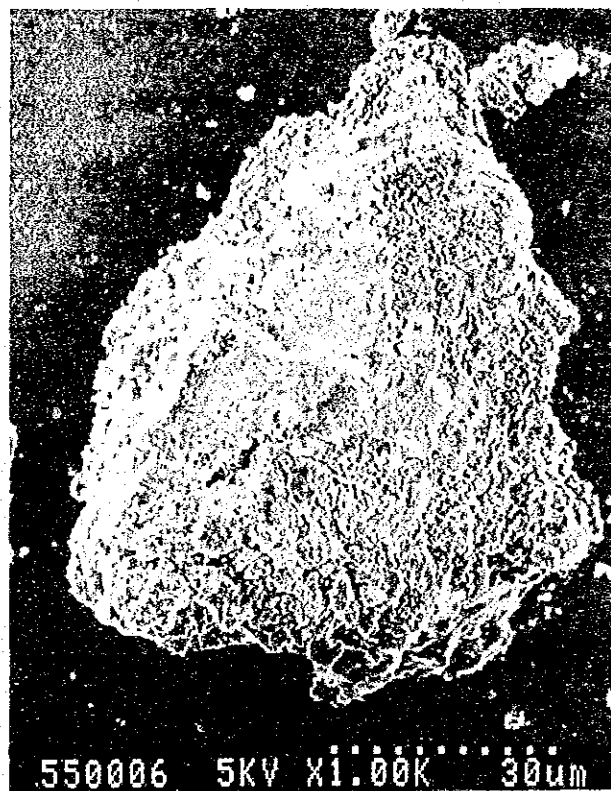


Fig.4.1.3. Result of SEM Examination of Scale Constituent Precipitated(Temp. 95°C, Retention Time 5 min., Scale Inhibitor Concentration 5ppm, Oil Concentration 100ppm)

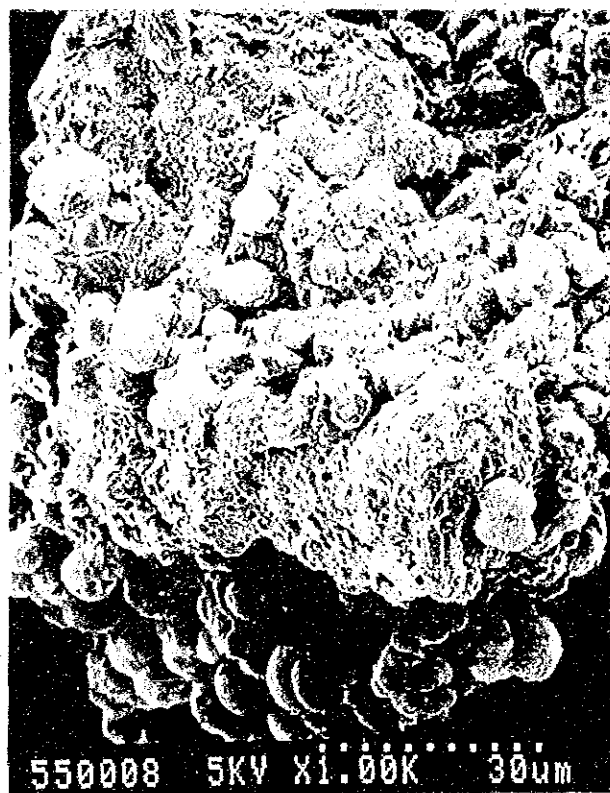
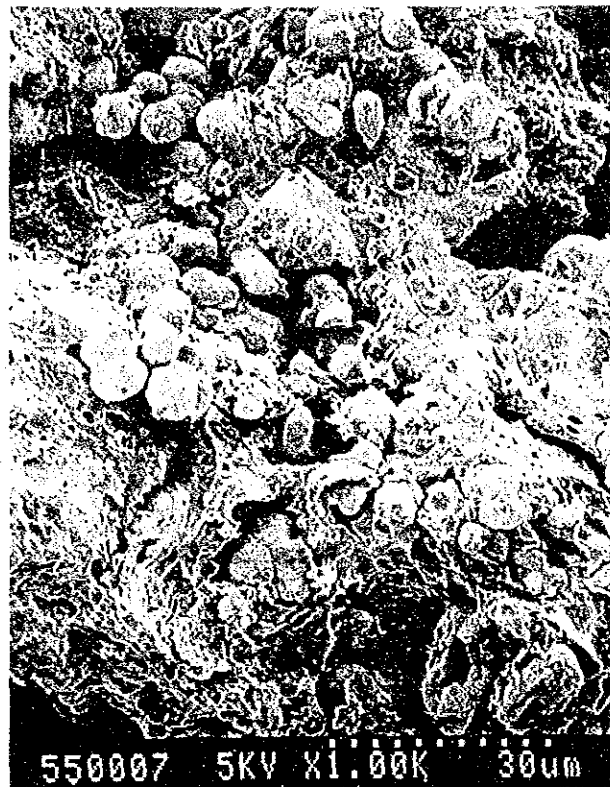


Fig.4.1.4 Result of SEM Examination of Scale Constituent Precipitated(Temp. 95°C, Retention Time 17 min., Scale Inhibitor Concentration 5ppm, Oil Concentration 100ppm)

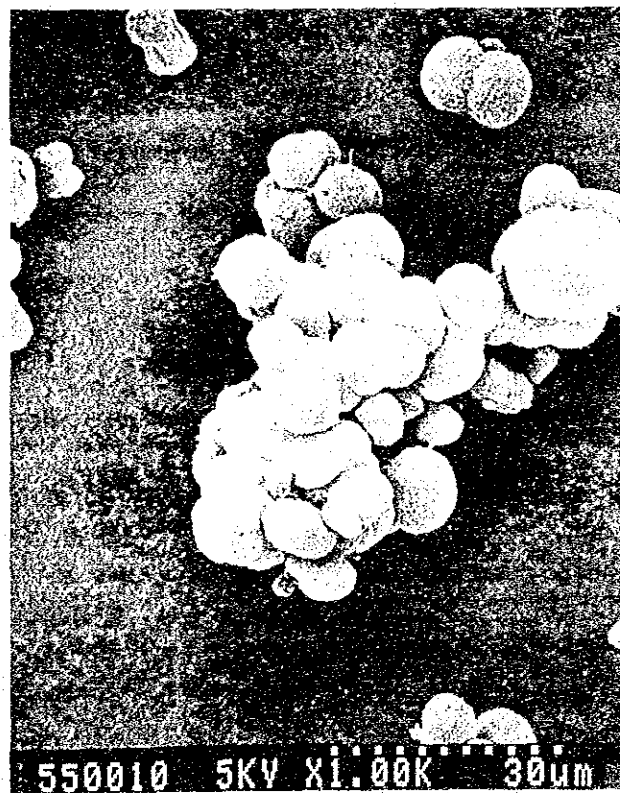


Fig.4.1.5 Result of SEM Examination of Scale Constituent Precipitated(Temp. 95°C, Retention Time 60 min., Scale Inhibitor Concentration 0ppm, Oil Concentration 0ppm)

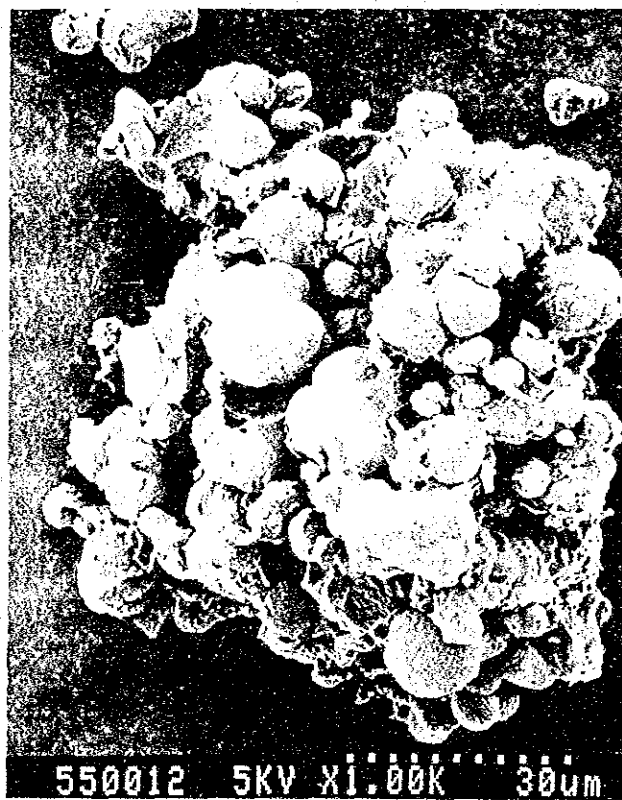
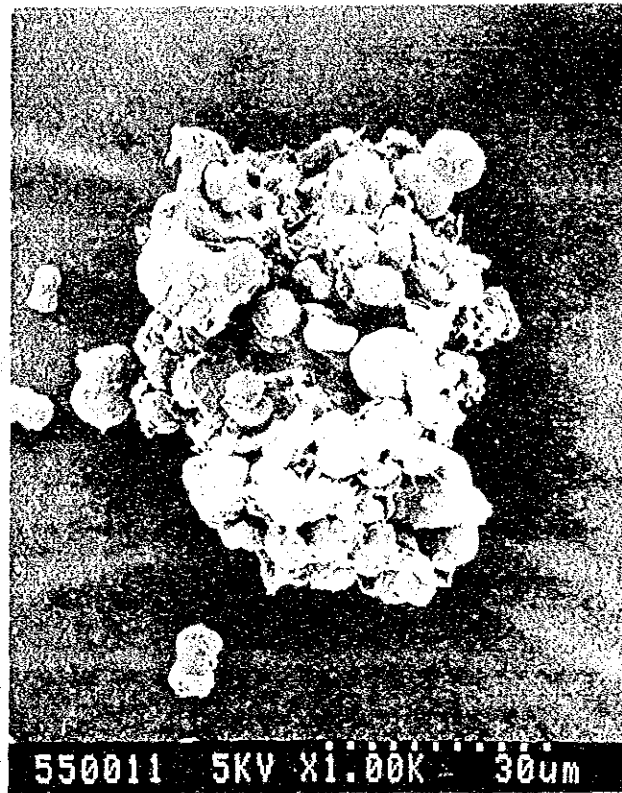


Fig.4.1.6 Result of SEM Examination of Scale Constituent Precipitated(Temp. 95°C, Retention Time 60 min., Scale Inhibitor Concentration 5ppm, Oil Concentration 0ppm)

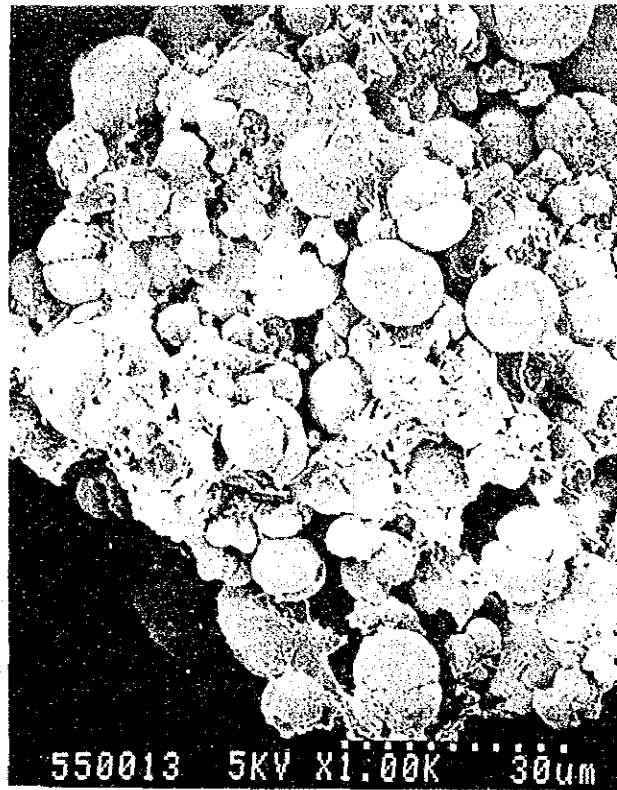


Fig.4.1.7 Result of SEM Examination of Scale Constituent Precipitated(Temp. 95°C, Retention Time 60 min., Scale Inhibitor Concentration 5ppm, Oil Concentration 100ppm)

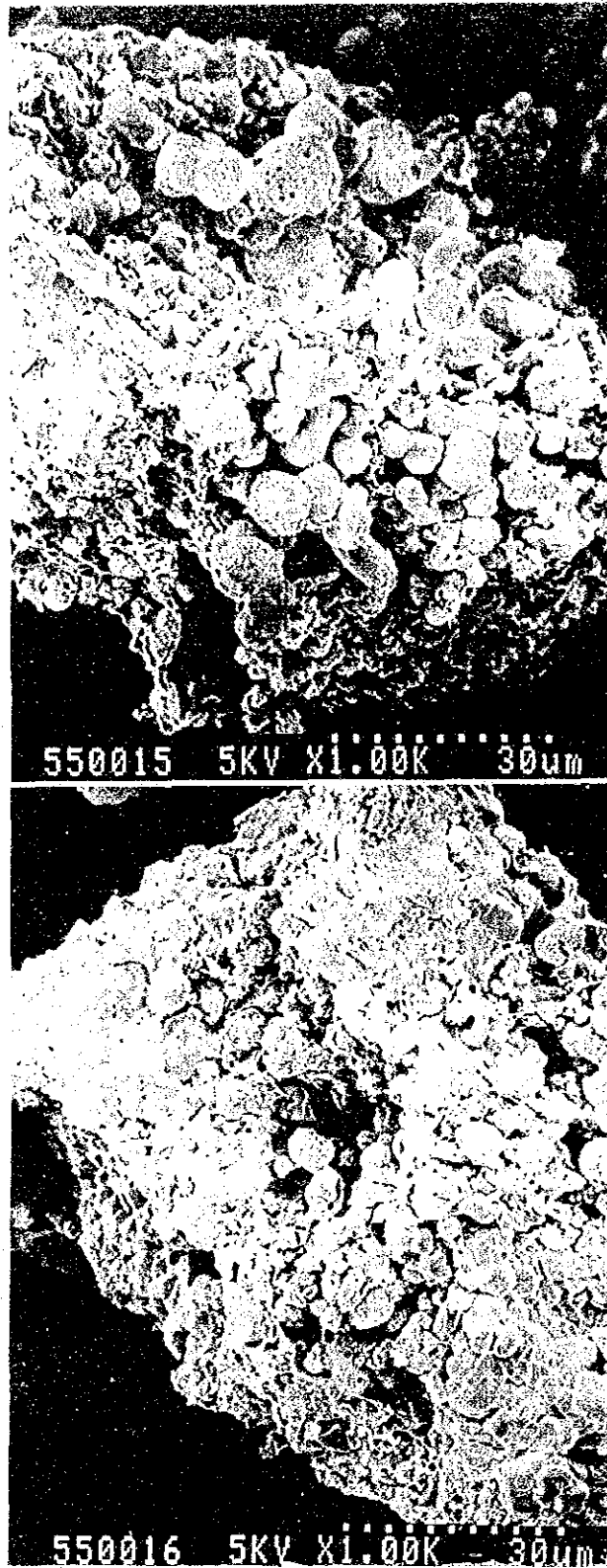


Fig.4.1.8 Result of SEM Examination of Scale Constituent Precipitated(Temp. 80°C, Retention Time 60 min., Scale Inhibitor Concentration 5ppm, Oil Concentration 100ppm)

precipitation which is stoichiometrically calculated. Though it is difficult to estimate the amount of CaCO_3 precipitation from this change in M-alkalinity using data which have been gained with a test unit where fluid continuously flows in and out, it becomes possible in case of a batch test unit like that for this experiment where the amount of charged brine is known.

B) will be discussed afterward, based on the results of SEM examination, since it can not be demonstrated in this research. A) can be confirmed by the analysis of water quality.

From the above viewpoints, residual M-alkalinity for each influence factor has been summarized, looking upon that the amount of precipitation corresponds to the value which is calculated by deducting residual M-alkalinity after the occurrence of precipitation from that at the time of the charging of brine. Figs. 4.2.1 to 4.2.4 show summarized results.

4.2.2 Evaluation of Various Kinds of Influence Factors by M-alkalinity

(1) Influence of Retention Time of Scale Inhibitor on M-alkalinity (ALK_F)

Fig. 4.2.1 shows the relationship between ALK_F (M-Alkalinity to be corrected of filtrate) and retention time at 5, 17 and 60 min. after the moment when precipitation has forcibly been formed by adding 1N Na_2CO_3 to brine which was added with a scale inhibitor of five ppm beforehand. (Initial alkalinity is 1,000 + 181.7 ppm as CaCO_3)

When comparing the blank value at 5 min. after with the value when a scale inhibitor of 5 ppm was added, ALK_F of the latter is larger and it means that this scale inhibitor has slowed down the growth of precipitation. However, when oil is added, the growth speed of precipitation increases (the reduction rate of M-alkalinity increases). When oil of as much as 100 ppm is added, the reduction rate of M-alkalinity increases up to nearly three times of that in the case of no added oil.

On the other hand, as retention time becomes longer, the difference in M-alkalinity mentioned above becomes smaller gradually and, 60 min. after, M-alkalinity values under all conditions converges in around 100 ppm as CaCO_3 . In other words, both the scale inhibitor and oil are hardly concerned in precipitation stoichiometrically, and the former in particular supports the established theory. For oil, it can be said that the above-mentioned fact has also been confirmed by this experiment from the fact that oil has no affinity with water under this temperature, though it has already been anticipated.

When looking only data of 60 min. after, the presence of oil has no relation to the occurrence of precipitation and the effect of the scale inhibitor can be said to be only the effect of crystal distortion. Actually, the above-mentioned state is impossible, since the retention time of circulating brine is two to three minutes in actual plants of 20,000 t/d class. Data of 5 min. after therefore seem to be the most important.

Needless to say, the occurrence of precipitation does not directly connect with the

increase of fouling index and the rate of scaling to heat transfer surfaces slows down when the crystal distortion effect effectively works, even if precipitation has occurred. However, the occurrence of precipitation is always the primary factor for the increase of fouling index and it is important to look the influence of oil whether or not it can be the initiation of precipitation.

When evaluating data of 5 min. after from such a viewpoint, it can be said that the presence of oil in actual plants with retention time of two or three minutes becomes the cause of accelerating precipitation and higher oil concentration accelerates more.

As can be seen from Fig. 4.2.5, S. Steinberg et al⁵ shows that the amount of circulating brine containing a scale inhibitor, i.e. retention time, closely relates to the growth rate of precipitation and the latter acceleratedly increases with the increase in retention time. This trend is similar to this experiment.

It is easily anticipated that the rate of increase in the growth speed of precipitation with the increase in retention time varies according to the kind of inhibitors.

(2) Influence of Concentration of Scale Inhibitor on M-alkalinity

Fig. 4.2.2 shows the correlation between the residual M-alkalinity and the concentration of scale inhibitor added at five minutes after the scale inhibitor comes into contact with precipitation under the conditions of oil concentration 100 ppm and 95°C. It is clearly seen from this figure that the inhibitor of more than 3 ppm has no effect to prevent precipitation. This value perfectly coincides with the concentration of scale inhibitor added of 3 or 4 ppm in Al Jubail Phase-2 plants. This fact has unexpectedly proved that scale prevention has been carried out effectively and economically in these plants. This fact has also proved the adequacy of this evaluation method.

(3) Influence of Temperature on M-alkalinity

Fig. 4.2.3 shows the correlation between temperature and M-alkalinity at 60 minutes after the scale inhibitor comes into contact with precipitation under the conditions of the concentration of scale inhibitor 5 ppm, and the same of oil 1 and 100 ppm, together with blank values. These data have been obtained by the 60 min. test which has been conducted without anticipating that the contacting time of the scale inhibitor with precipitation has so large influence on M-alkalinity. The 5 min. test should therefore be conducted separately. However, this test has not been conducted because scaling becomes an issue only in high temperature state, data from this test have already been obtained as described in 5.2.1 and considerably long time is needed for preparing brine.

The following can be concluded from the above-mentioned data.

- 1) Though the influence of oil is not so large under the conditions of retention time 60 min. and 50°C, the higher concentration of oil still lowers residual M-alkalinity and accelerates the growth of precipitation.
- 2) Under the conditions of retention time 60 min and 80°C, the decrease in M-alkalinity is similar to that at 50°C when oil is not included. However, the higher the concentration of oil is, the larger the decrease in M-alkalinity becomes in comparison with that at 50°C when oil is included.
- 3) Under the conditions of retention time 60 min and 95°C, the effects of scale inhibitors and the influence of the concentration of oil completely disappear, and the decrease in M-alkalinity is accelerated.

(4) Influence of Oil Concentration on M-alkalinity

Fig. 4.2.4 shows correlations between residual M-alkalinity and the concentration of oil for retention times of 5 min. and 60 min. by temperature. Evaluation on these results has already been described in (1), (2) and (3).

However, reference should be made to the fact that the particle size of precipitation becomes very small when oil of 100 ppm is added. Some particles of precipitation have passed through No. 5C filter paper at the test under the conditions of oil concentration 100 ppm, temperature 80°C and retention time 60 min, as mentioned in (3). This fact is considered to be the reason for the abnormal value of residual M-alkalinity of filtrate under the condition (S204) of this experiment. (Filter paper of 0.45 micron has been used for the test under the conditions of 95°C, 100 ppm and 60 min. <S104>).

Consequently, these data were plotted at the time the figures were made, but they have been neglected when related lines were made.

4.2.3 Effect of Scale Inhibitor on Crystal Distortion

The shapes of crystals have been compared for both cases where oil was added and not added, and from the results of SEM photographs of precipitate which have been obtained during the experiments conducted under the conditions shown in Table 4.1.2. Though the shapes of crystals have scarcely been changed by the addition of oil of about 1 ppm, they have been changed to an aggregate of spherical shapes with diameters of about over 100 μm by the addition of oil of 100 ppm. Furthermore, the shapes of crystals have also been observed in the preliminary experiment when oil of 1000 ppm has been added. As shown in Fig. 4.2.6 and 4.2.7, particles with diameters of about 100 μm down to 30 μm or smaller were found.

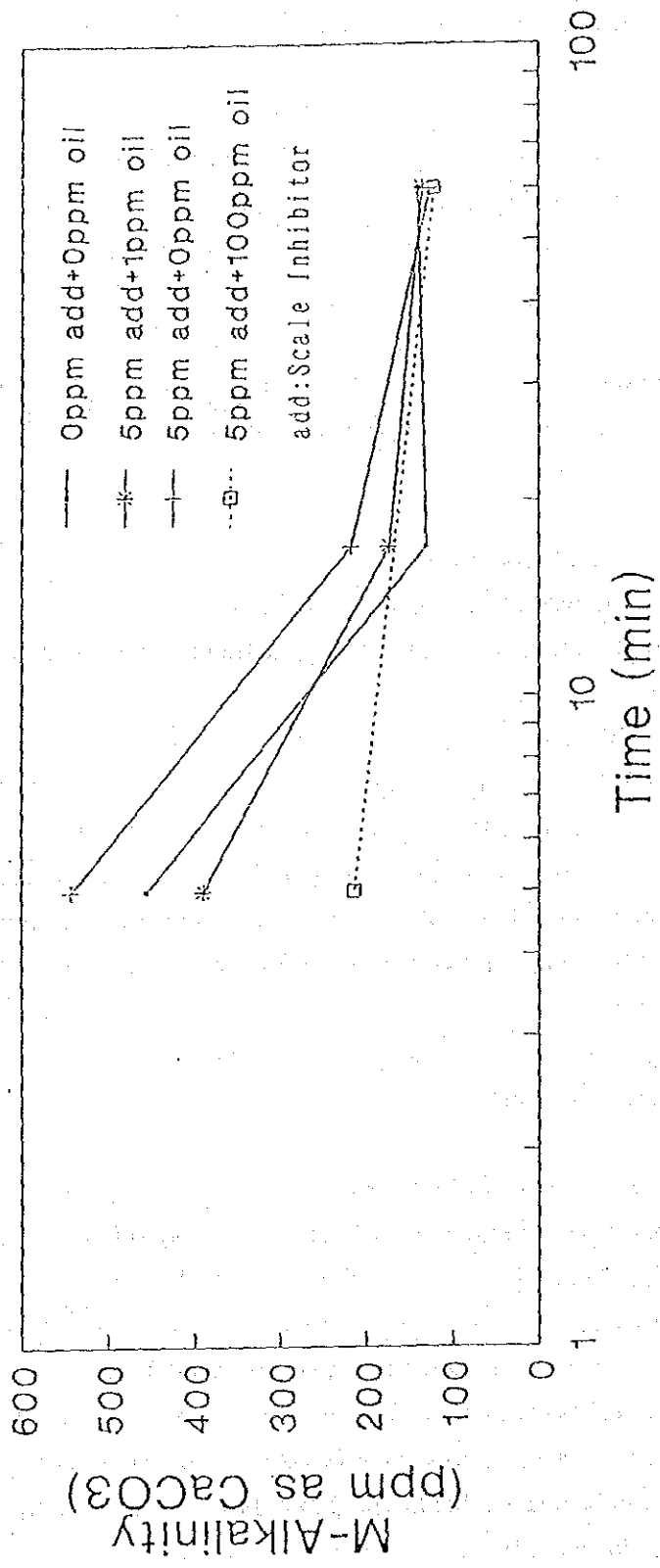


Fig.4.2.1 Effect of Retention Time on M-Alkalinity(95°C)

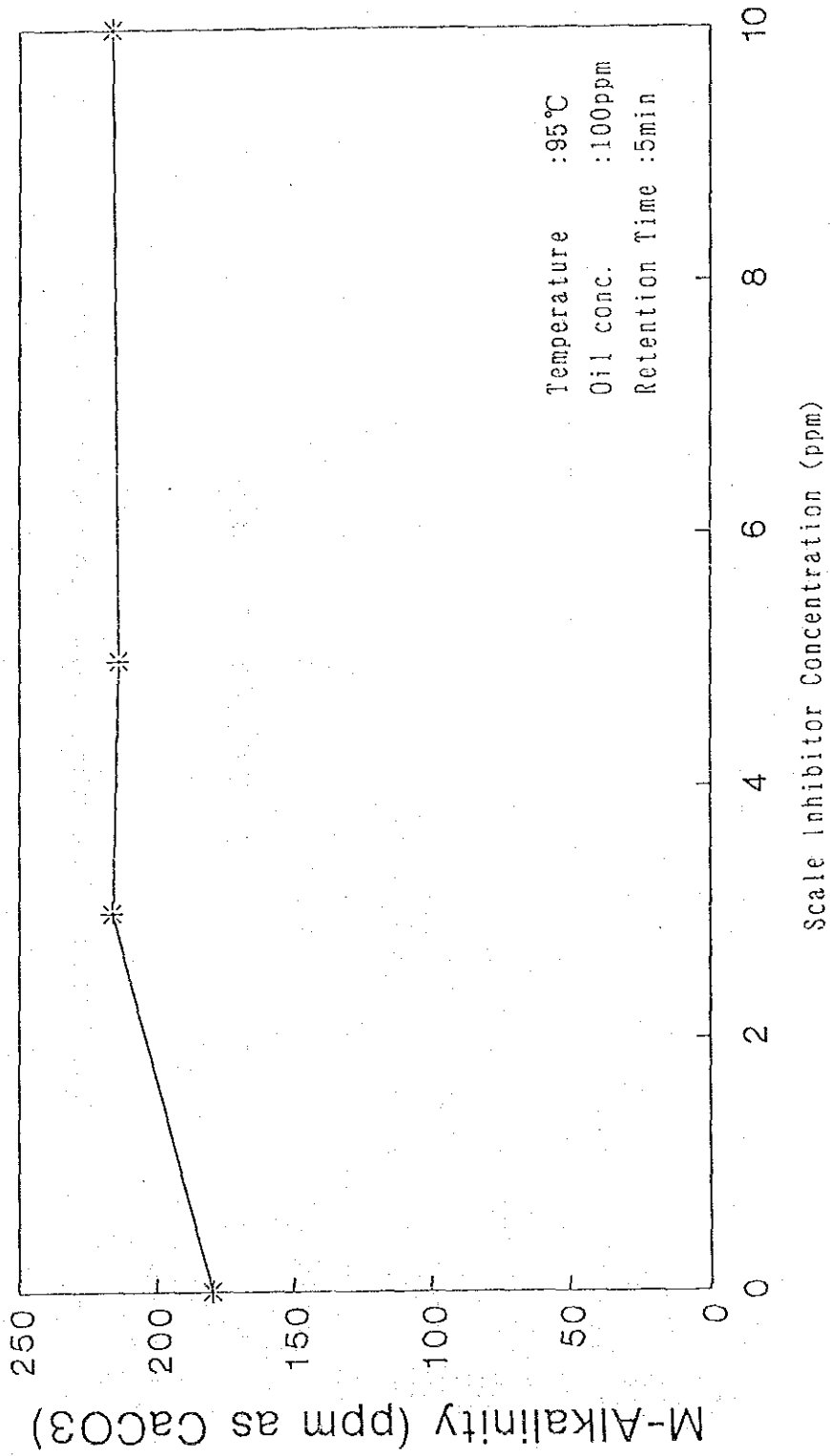


Fig.4.2.2 Effect of Scale Inhibitor Concentration on M-Alkalinity

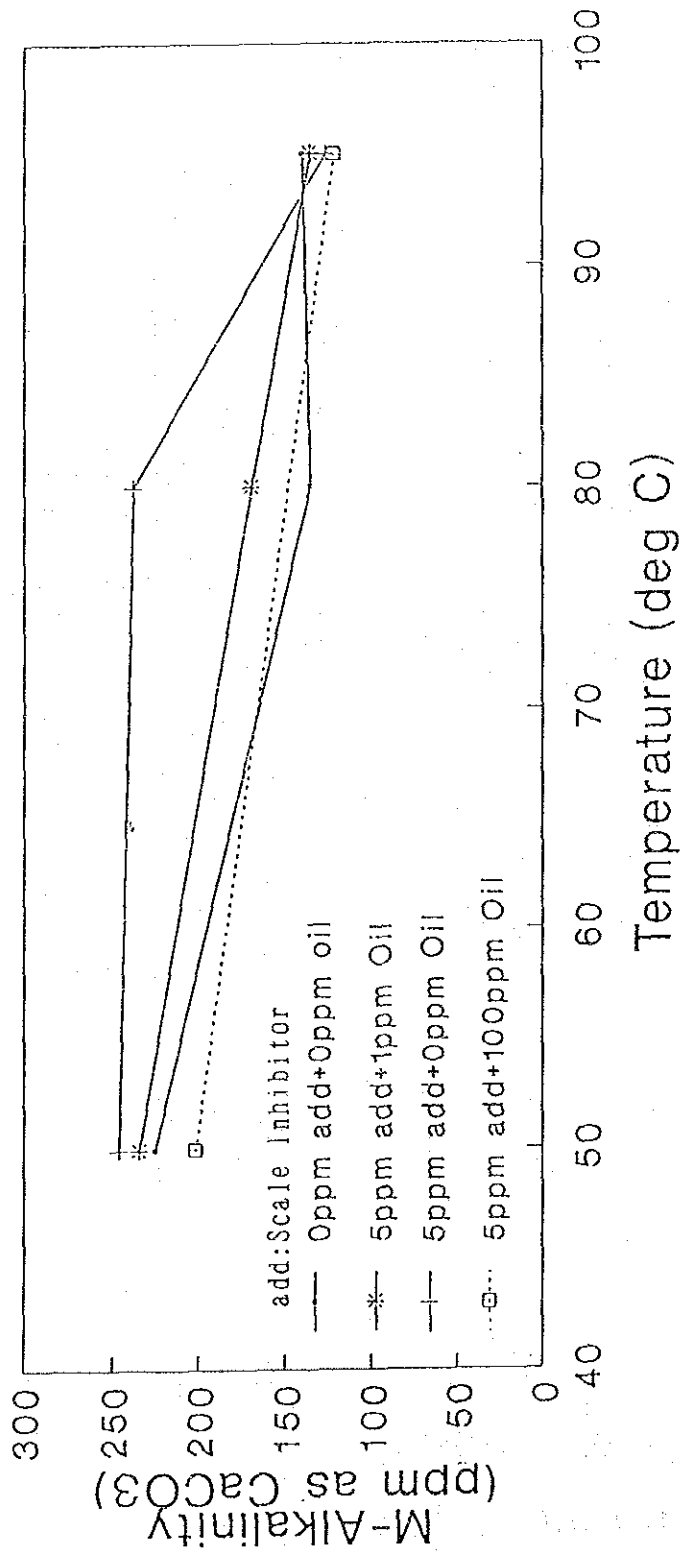


Fig.4.2.3 Effect of Temperature on M-Alkalinity(Retention Time: 60min)

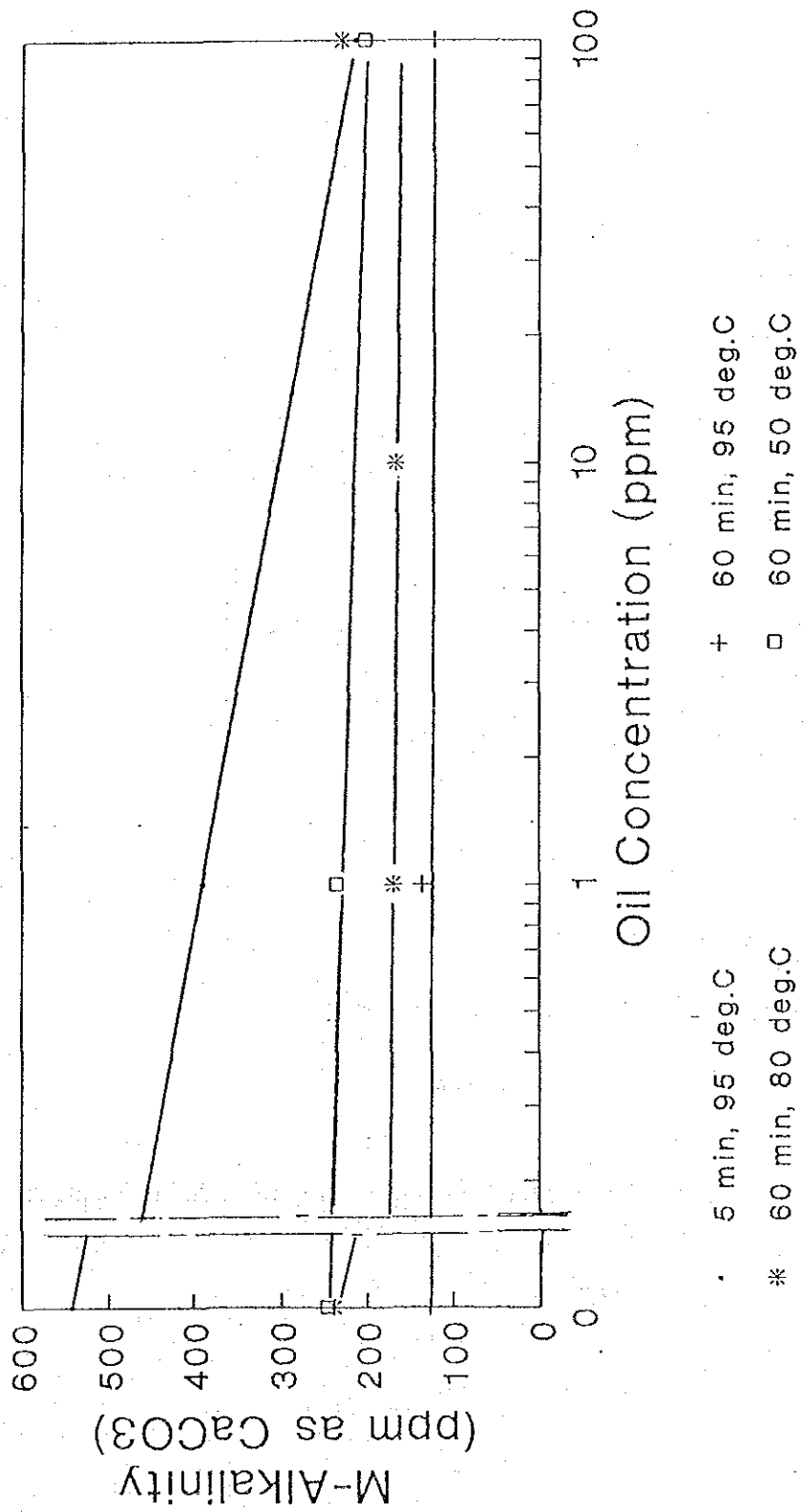


Fig.4.2.4 Effect of Oil Concentration on M-Alkalinity(Scale Inhibitor Concentration: 5ppm)

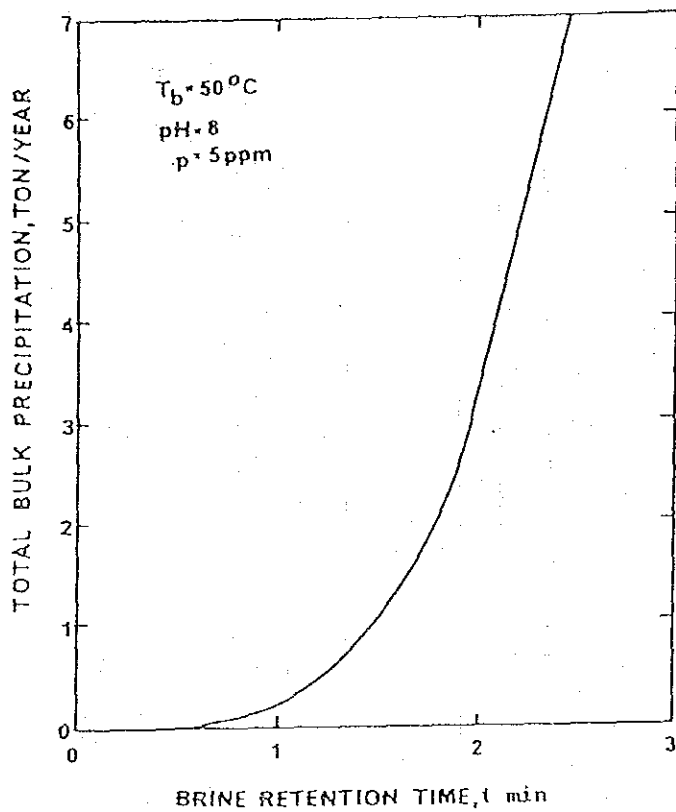


Fig.4.2.5 Effect of Retention Time on Quantity of Scale Precipitated⁵

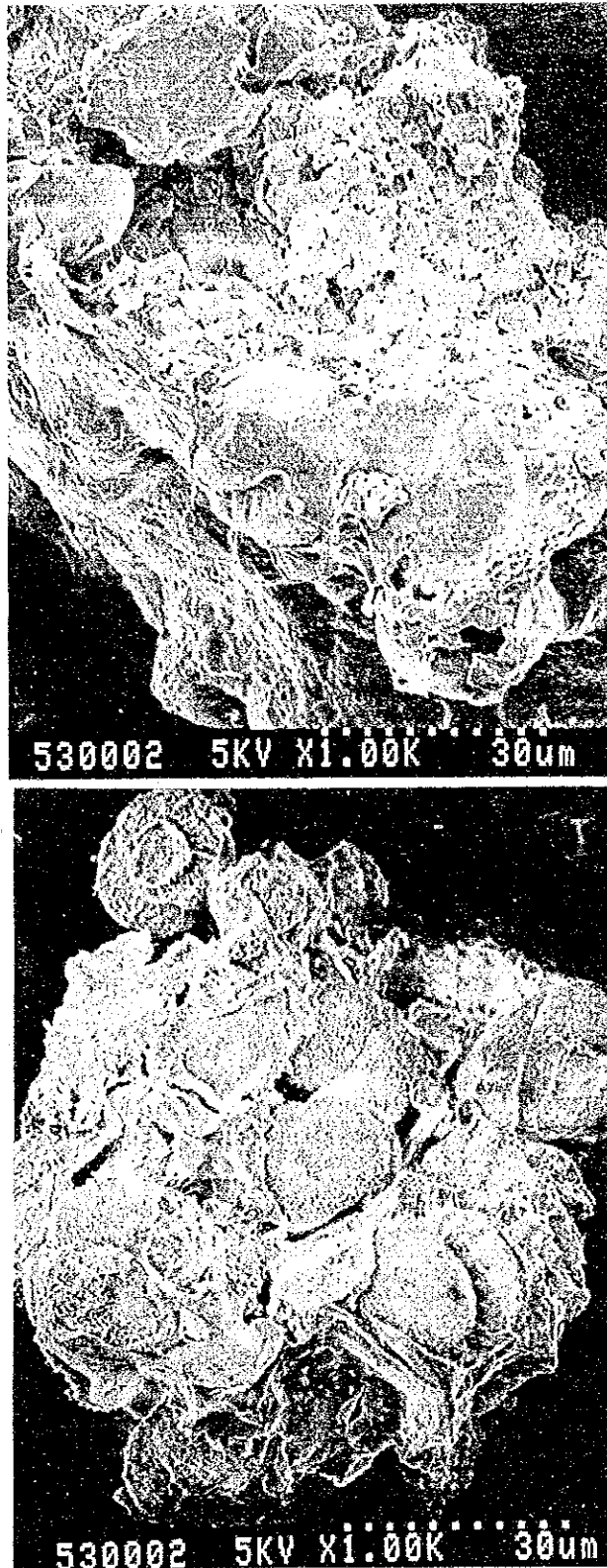


Fig.4.2.6 Result of SEM Examination of Scale Constituent Precipitated(Temp. 95°C, Retention Time 60min., Scale Inhibitor Concentration 5ppm, Oil Concentration 0ppm)

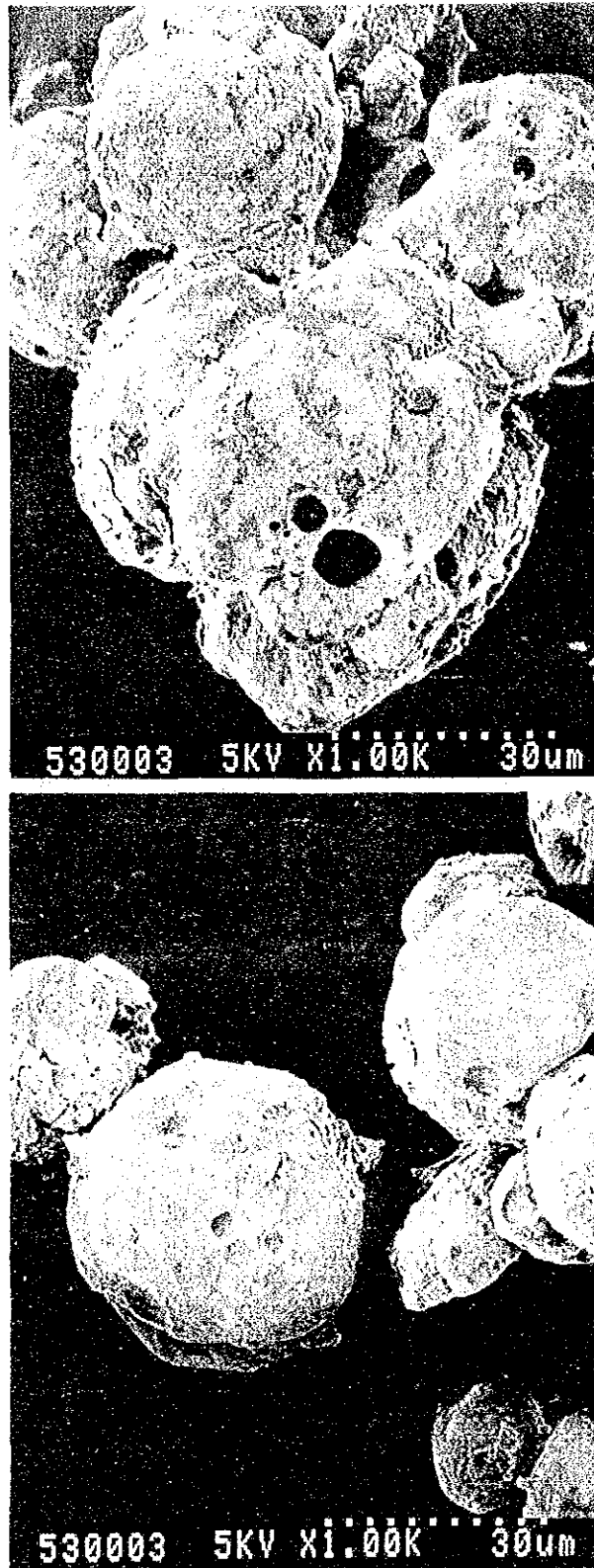


Fig.4.2.7 Result of SEM Examination of Scale Constituent Precipitated(Temp. 95°C, Retention Time 60 min., Scale Inhibitor Concentration 5ppm, Oil Concentration 1000ppm)

However, though particles were found down by the intrusion of oil, this phenomenon does not directly connect with the adhesion of oil to inside surfaces of heat transfer tubes. Experiments with bench-scale equipment which imitates the heat transfer conditions of MSF are necessary to clarify this connection.

For the effect of a scale inhibitor, clear difference has not been found through photographs which have been taken this time. However, clear difference in the adhesion of precipitation to the inside surfaces of the three-neck flask has been found during the experiment between two cases where a scale inhibitor has been added and it has not been added. When a scale inhibitor has been added, precipitation has scarcely adhered. Quantitative data, however, could not be obtained through this experiment.

In any case, bench-scale equipment mentioned above is preferable to the present Batch-type experimental equipment in order to give universality to these data.

5. Conclusion

Experiments and investigations have been conducted on the relationships between the inhibiting effects of scale inhibitors and each of the concentration of oil, retention time (reaction time), temperature, and the concentration of inhibitors by excessively adding carbonate ion. This experiment is different from practice in general, by forcibly depositing scale in brine to clarify the change in the performance of scale inhibitors which are now used in actual plants when crude oil has intruded into raw seawater. Results acquired by these experiments are as follows.

- (1) The presence of oil is a factor that accelerates scaling and consequently the degree of scaling becomes greater for higher oil concentrations.
- (2) Polymeric carboxylic inhibitor "X" which has been used in this experiment, has the ability to suppress scaling when it comes into contact with brine under scale forming conditions. However, that ability diminishes time as reaction time is extended.
- (3) There was no difference in the inhibiting effect of scale inhibitor "X" on precipitation and deposition in the range of temperature tested when oil is included, even though more than 3 ppm of this inhibitor was added.

6. Future Subjects

In this experiment, the amount of foulants were evaluated from the results of a decrease

in M-alkalinity by primarily grasping the generation of foulants when grasping the phenomenon of scaling in MSF. However, all "scaling substances", i.e. precipitation, do not necessarily adhere to heat transfer tubes as scale. Concentration gradients in the vicinity of heat transfer surfaces are necessary for the adhesion of scale and they allow the phenomenon of scaling to be related to the concept of fouling. This is most important for the stable operation of MSF over a long term. Also, there is a close connection between the difficulty in removing scale by ball cleaning and a decrease in the fouling factor.

From the above-mentioned viewpoint, a long-term experiment under various conditions changing the kind and concentration of oil and the kind of scale inhibitor is considered necessary as the next stage of research to clarify the decrease in heat transfer coefficients (increase in the fouling factor of a heat transfer tube) when oil has intruded into raw seawater.

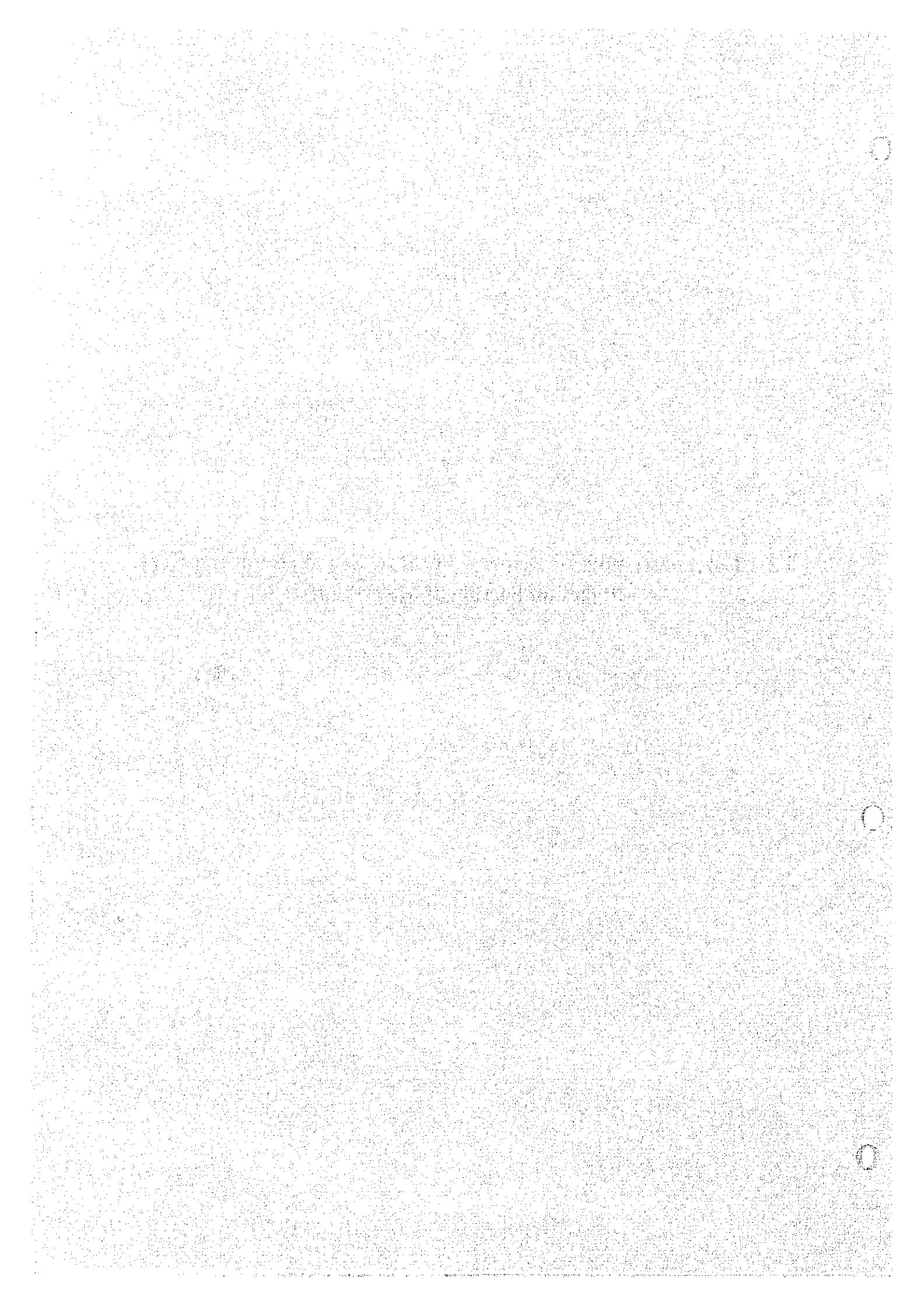
Though it can be thought to use a test plant directly for these experiments in a heat transfer state, a complicated process such as the cleaning of the inside of equipment when experimental conditions are changed is necessary, since oil is introduced into the test plant.

If contingency planning is necessary in SWCC, it is considered that bench-scale tests using equipment which has heat transfer surfaces should be carried out and then confirmation tests using a test plant should be conducted after experimental conditions have been strictly selected through bench-scale tests.

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**3.2 M-4 Analysis of Oil Dispersed in Raw Sea Water at the Heat
Rejection Section of MSF Plant**



**MSF DESALINATION
EXPERIMENTAL RESEARCH NO.2, M-4**

**ANALYSIS OF OIL DISPERSED IN RAW SEAWATER
AT THE HEAT REJECTION SECTION OF MSF PLANT**

**"The Course of Petroleum Hydrocarbons from Diesel Fuel Oil
in MSF Plants: Evaluation of TOC, IR, and GC/MS Methods
for Analysis of Oil in Brine Streams"**

JULY 1992

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1. Introduction

In the Arabian Gulf, contamination of seawater by oil has become a matter of growing concern. In particular, oil outflow during the Gulf War had posed serious problems to seawater desalination plants. In the situation, if oil contaminated seawater is used as raw water for the MSF evaporation type desalting process (i.e. the main desalting process used in the region), part of oil may be carried over in the product water, thereby rendering it unsuitable for drinking.

There are several barriers to overcome in counteracting oil pollution of seawater in order to obtain water from a contaminated seawater outflow. Various methods are available for trial to prevent oil mixed with the seawater, as it is extremely important that seawater contaminated with oil, should not be supplied to the MSF plant equipment. However, even if utmost precautions are taken, the oil is not always totally removed and possibility of a certain level of oil mixed with the seawater always exists.

In order to devise countermeasures to protect the internal equipment of the MSF plants, together with developing an understanding of behavior of oil in flash chamber and evaluating its effects on the quality of the product water, it is necessary to develop a method of analysis of oil in seawater and product water.

Moreover, it is important to survey the relevant data to study several phenomena (particularly evaporation of water and evaporation/condensation of oil which occur in parallel with it) which occur concurrently within the plant. During quantification, if the composition of the oil present in seawater is simple, it is possible to simulate it by chemical engineering analysis. However, in fact, the properties of the oil present in seawater are extremely complicated and are extremely difficult to quantify.

Therefore, to cope with the flow of oil into the Arabian Gulf, the purposes of this study are set up as follows:

- (1) To compare three methods currently available for the analysis of oil contained in seawater, concentrated brine and desalted product water.
- (2) To conduct a basic experiment for measuring the amount of oil-contaminated seawater transferred into product water (at the desalination plant of the Al-Jubail phase 2)

2. Literature Survey

First of all, it is essential to establish a firm grasp of the most up-to-date technology and collect references and assemble all of the available technological data published to date. Together with this, it is necessary to clearly define the method for measuring the concentration of oil present in the product water, seawater and brine necessary for clarifying phenomena, whereby

the oil, which is introduced into the evaporation chamber, is evaporated and redissolved in the product water. Then, based on these results, make comparative experiments on a laboratory-scale to determine the amount of oil, present in the brine, which passes into the product water. Thus, acquiring the fundamental data for conducting the demonstration experiments on the 20t/d MSF Test Plants effectively and expediently, which will form the next stage of the research.

2.1 Method of Investigation

- (1) To survey the most suitable analytical method for oil present in product water, seawater and brine,
- (2) To survey the information on behavior of contaminants, particularly oil, in an MSF plant.

The principal data bases used for the research survey are listed below.

JOIS (JICST Online Information System)

DIALOG

Other available sources

2.2 Result of Investigation

In order to obtain information that are of use to evaluate the quality of the desalination plant product water and investigate the countermeasures of the plant equipment when the feed-water to the desalination plant is contaminated with spilled oil, literatures published since 1980 using the on-line data base such as JOIS or DIALOG have been surveyed.

Many literatures have been picked up for the key words "Desalination" and "Contamination". Almost all of them were on the radioactive contamination when desalination plants were in combination with the nuclear power plant. Several literature which meet the objects of this work have been looked up. The abstract is attached in the appendix.

Every literature is of value for reference to the objects of this work. The most comprehensive report was the "Countermeasures against oil contamination of seawater desalination plant by MSF"¹ published by Water Re-use Promotion Center, Japan. None of them gives any calculation methods and experimental data with which it is possible in the generality of cases to evaluate the oil quantity transported from the evaporating brine to the condensate in the process of seawater distillation.

So, experiments and investigation for this subject are considered to be very important.

3. Experiment

3.1 Experimental Apparatus Set Up

The experimental set up for this work is shown in Fig. 3.1.1. The system consists of a rotavapour, heating oil bath, a closed loop cooling system, vacuum pump capable of creating vacuum up to 47.5mmHg and Hg manometers. A matrix of concentrated seawater into which oil was spiked was prepared by evaporating 1000 ml of filtered seawater of the Arabian Gulf to approximately 600 ml. An exact concentration ratio of 1.4 was maintained by dilution with demineralized water. For blank test 500 ml concentrated brine was refluxed to 95°C with condenser circulating water temperature 10°C by a refrigerated constant temperature circulator. Then 630 mmHg vacuum was created in order to flash brine inside the flask when the system was equilibrated, and the distillate was collected for 10 min. Then brine was cooled down to 80°C and was allowed to flash at 350mmHg. It was further cooled to 50°C and flashed at 90mmHg pressure. The temperatures and vacuum were created to simulate MSF conditions in 1st, 5th and 15th stages of evaporators. Approximately 20 ml of distillate was collected under each conditions.

Calculated amounts of heavy oil was mixed with the concentrated seawater in order to get oil concentrations of 10, 50 and 100 mg/l in 500 ml brine for the actual experiments. The flashing from the brine were collected and the distillate fractions were analyzed for oil by total organic carbon analyzer, infrared oil meter and gas chromatography/mass spectrometry. To start with the distillate from each experiment was divided for TOC, IR and GC-MS analyses. The analytical results so obtained were found to be unacceptable due to the non-homogeneity of the fractions. Later the entire distillate was used for GC/MS analysis including the rinsing of the receiving flask of rotavapour with methylene chloride. For TOC and IR analyses separate experiments were done. Only 1 ml of thoroughly mixed samples was drawn for TOC. The concentrated brine left in distillation flask was analyzed by GC/MS and IR. The brine fraction was not analyzed for TOC due to high salt contents that cause poisoning of the catalyst in the TOC equipment.

The results of elemental analyses of the oil used during this study are listed in Table 3.1.1. The highest limit posed in Japan for sulfur concentration in fuel oil is 2%. A concentration of 1.6% S further confirms that this is a fuel oil used in various industries in Japan.

Table 3.1.2 shows pH, electrical conductivity and chloride concentrations of concentrated brine (concentration ratio = 1.4) used during the entire work. The chloride concentration of Arabian Gulf water is 23500 mg/l and electrical conductivity 59,000 μ s/cm. Concentrated brine was used in order to match the composition of recirculating brine in actual MSF desalination plant conditions.

3.2 Analytical Methods

Analytical techniques selected for this study were based on well recognized methods

Table 3.1.1 Average Elemental Determination of Diesel Fuel Oil

% C	% H	% N	% S
87.5	11.4	ND	1.6

ND= Not Detected

Table 3.1.2 Quality of Brine Before and After Tests

Parameter	Before	Brine After Tests		
	Test	10 mg oil/l	50 mg oil/l	100 mg oil/l
pH	8.08	8.49	8.63	8.41
EC(μ s/cm)	7.83×10^4	8.58×10^4	8.37×10^4	8.54×10^4
Cl ⁻ (mg/L)	32,900	NA	NA	NA

NA = Not Analyzed

using TOC, IR and GC/MS analyzers for characterization of organics especially oily matter in water.

- (1) Total Organic Carbon: The total organic carbon analysis was performed by Shimadzu TOC Analyzer model TOC-500 using NDIR detector by total carbon and inorganic carbon difference method.

Conditions : TC oven temp. 650°C, IC oven temp. 160°C, carrier gas flow 150 ml, dual channel NDIR detector.

- (2) Total Oil Analysis by IR : Total oil in brine, water fractions collected at 95°C, 80°C, 50°C and concentrated brine left in flask was determined by extraction method using carbon tetrachloride. The extracted oil was measured by Yanaco potable oil meter 103 with non-dispersive infrared analyzer whose selectivity is set at 3.4–3.5 μ m of wave length. Octane,

cetane, benzene (OCB) have been used as standard.

- (3) Volatile Aromatics : Volatile aromatics present in the heavy oil were analyzed by purge and trap method. Known amount of oil was mixed in brine, vigorously shaken for about 2 minutes and 5 ml of brine was purged with helium gas for 10 minutes using Tekmar model LSC2 liquid sample concentrator connected to Hewlett Packard gas chromatography model 5880. The volatile organics adsorbed on a 30 cm tenax column were desorbed at 180°C and injected directly in the gas chromatographic column through a sample splitter.

Hewlett packard model HP 5880 gas chromatography with Flame Ionization Detector (FID) was used for detection and HP integrator was used for the quantification of volatiles. Supelco volatile organics standards were used for quantification. Fused Silica capillary column VOCOL, 30 m x 0.53 mm I.D., film thickness 3.0 μ m was used for volatile components separation with GC conditions: Injector temperature 240°C, detector temperature 250°C, initial column temperature 35°C for 4 minutes and then raised to 200°C at the ramp rate of 4°C/min. 10 ml/min helium and 30 ml/min nitrogen were used as carrier and make up gases, respectively.

- (4) Total Oil by GC/MS: The distillates, and concentrated brine obtained at 95°C, 80°C and 50°C experiments were extracted with methylene chloride using a separatory funnel. The methylene chloride extract was dried on anhydrous sodium sulfate and concentrated as per the requirements. After each extraction water volume was measured for the purpose of concentration calculations. USEPA method No.625 has been employed to determine the extractable organics during this work with slight modifications. The extracted oil was analyzed by gas chromatography HP 5880 and MSD model 5970 coupled to 7914 data system with double disc drive computer HP 9000/236. MSD operating conditions: Scan m/z 50-500, scan threshold 15, solvent delay 2.2 minutes, dwell time 2 ms/ion.

The mass spectrometer was operated in selected ion mode (SIM) with dwell time 100 ms/ion for monitoring of m/z 57, 77 and 178 for hydrocarbons, substituted phenyls and polycyclic aromatic compounds, respectively, in order to perform qualitative analysis oil alone.

GC Operating Conditions : Fused silica capillary column HP 1.30m x 0.50 mm I.D., 0.30 mm film thickness interfaced directly to MS ion source. Helium gas flow through column was 1 ml/min.

Temperature program : initial temp. 50°C, hold 3 minutes, ramp at the rate of 10°C/min up to 250°C, hold 17 minutes, injector temp. 200°C, GC/MS interface temperature 280°C. The identification and quantification of the distillates were done using standard heavy oil mixture.

4. Results and Discussion

4.1 Evaluation of the analytical methods for oil

Table 4.1.1 shows data on the determination of total oil by three different methods i.e., TOC, IR and GC/MS. TOC determination was made by direct injection of oil impregnated water, however, IR and GC/MS determinations were done by carbon tetrachloride and methylene chloride extractions, respectively. Examination of this data reveals anticipated wide range of fluctuations in TOC determinations. The accuracy of this method appears to be questionable. Moreover, determined concentration of oil by this method remained lowest compared to IR and GC/MS methods in 50 mg/l and 100 mg/l experiments. The possible reason of low concentration by this method may be attributed to floating oil on the water surface which could not be taken by sampling syringe during analysis. In fact, the oil analyzed by this method is largely dissolved in water column or emulsified oil after shaking samples prior to the analysis.

Table 4.1.1. Evaluation of Analytical Methods for Oil

mg/l oil in brine	Method	Analytical Oil mg/l in collected fractions Conc.			
		95°C	80°C	50°C	Brine
10	TOC	3.0	0.94	4.02	NA
	IR	0.6	2.5	1.1	0.7
	GC/MS*	19.1	6.29	2.75	0.90
50	TOC	73.0	17.3	23.3	NA
	IR	193.1	97.7	75.2	11.33
	GC/MS*	146.9	146.05	61.6	3.35
100	TOC	285	78.2	69.8	NA
	IR	445	351	273	9.63
	GC/MS*	537	453	245	7.55

* Average

A comparison between IR and GC/MS analyses revealed edge of the latter on the former. However, determined concentrations by both methods were in very close proximity. It was found that highest concentration of oil was extracted in first fraction (95°C) followed by second fraction (80°C) and third fraction (50°C). Lowest oil concentration was recovered in the concentrated brine which is negligible compared to the oil distilled over. Fig. 4.1.1 shows average transfer of oil at different temperatures and concentrations. It could be easily seen that in all concentrations maximum oil was transferred in the distillate at 95°C followed by 80°C and 50°C. The transfer rate was also found to be directly proportional to the concentration of oil.

Since gas chromatography/mass spectrometry remained the most widely used method for oil spill identification, it was decided to use GC/MS technique in the entire study. Two different columns, one for volatile aromatics and other for total oil fingerprint have been used in an effort to attain resolution the alkane fingerprint components of oil. For quantification of volatile aromatics flame ionization detector was used whereas for alkane fingerprint mass detector was employed. With GC/MS the quantification of individual n-alkane carbon number could be achieved whereas in case of IR determination, only total oil concentration is possible.

The identification of polycyclic aromatics, substituted phenyls and hydrocarbons in the parent oil was done by selected ion monitoring of m/z 178, 77 and 57, respectively. Fig. 4.1.2 shows a single polycyclic aromatic compound detected near 15.5 retention time. Similarly substituted phenyls (Fig. 4.1.3) were either absent or if present were in very low concentration. Fig. 4.1.4 shows reconstructed ion chromatogram of heavy oil in selected ion mode monitoring of m/z 57 and Fig. 4.1.5 shows the total ion chromatogram of oil sample in the scan mode. The chromatographic temperature program rate was deliberately set at faster rate to allow rapid analytical time due to project time constraints.

The chromatograms of original oil revealed a smooth distribution of n-alkane overriding unresolved complex mixture (UCM) material. On the UCM hump a series of resolved components throughout n-C₁₀ to n-C₂₁ boiling range could be seen. One dominant n-C₁₅ to n-C₁₇ chain n-alkane is a major feature of the both ion chromatograms in scan and selected ion monitoring mode (Fig. 4.1.4 and 4.1.5). Senn and Johnson⁽²⁾ have reported similar type of chromatogram of heavier distillate in kerosene-diesel fuel oil range. The presence of UCM well above the base line produced by a solvent blank is diagnostic for petroleum. If the UCM shows a maximum at above n-C₂₅ and another at about n-C₃₅ this is diagnostic for crude oil sludge residues. Our chromatograms clearly show that this should be heavy oil fraction of petroleum crude since apex of UCM is in between n-C₁₅ and n-C₁₇. Alkanes generally were accounted for the majority of hydrocarbons with no consistent preference to odd or even chain length observed.

Fig. 4.1.6 shows the methylene chloride extracted hydrocarbon distribution after oil was

mixed in water. The overall concentration in Fig. 4.1.6 is much lower than in Fig. 4.1.5 which was dissolved in methylene chloride.

To sum up the above, in this experiment, a comparison between three widely recognized methods³ (TOC, IR, GC/MS) for analysis of organic substances in water has been done.

Needless to say, for the comparison of analytical methods, the same sample should be used. However, in the case of water mixed with oil (i.e. two liquid phase), being heterogeneous, it is very difficult to take out the sample with exactly the same quality. Also, it is thought to be necessary for the sample to go through a certain thermal process. Taking these things into account, samples for each method have been prepared by conducting separate distillation and the comprehensive evaluation was made. As shown in Table 4.1.1. the values obtained by the IR method is roughly the same as those by GC/MS method, whereas the TOC values greatly differ from them, even if some fluctuations in the distillations for three methods are taken into consideration.

The TOC method is unsuitable for the samples containing water-insoluble organic substances such a case as in this experiment. This is due to the characteristic limitation for TOC that samples should be taken directly from inhomogeneous water-oil mixture rather than from organic solvent.

The result of the experiment indicates that both IR and GC/MS method could be applied to measure total oily matters in water. Among them, GC/MS method makes it possible to analyze not only total oil but also each oil constituents. Moreover, GC/MS method in which less toxic methylene chloride is used as extraction solvent rather than toxic carbon tetrachloride is superior to IR method.

4.2 Amount of transferred oil and oil concentration in distillate

Many competing factors such as temperature, vacuum, brine concentration and flow rate act concurrently to determine rate of transport of oil present in MSF feed water to product water. By measuring hydrocarbons in the different stages, calculations of over all transport of oil is possible. Results of simulated calculations of oil transport in product water from feeds containing 0.1-100 mg/l for Al-Jubail desalination plant have been presented (Water Reuse Promotion Center, Japan, 1991). As per the findings low boiling point component evaporate first and if external vacuum deaerator is installed majority will be vented out and where final stage deaeration system is installed chances of product water contamination by oil remain fairly good.

Since the oil used in this work was diesel fuel oil which is a heavy fraction of kerosene and diesel oil, therefore, does not contain components below n-C₉. It's due to this reason that benzene, toluene, ethyle benzene and xylenes (BTEX) were absent in the dissolved aromatic

hydrocarbon chromatogram (Fig.4.2.1) by purge and trap method. However, Kutty et al.⁴ have reported presence of benzene and toluene in seawater and occasionally in product water of Al-Jubail plant after Mina Al-Ahmadi crude oil spillage during the War in the Gulf. But the concentration never exceeded 0.1 mg/l.

In the laboratory test conditions three temperatures and corresponding negative pressure at which water could be flashed were selected for this study. The brine was allowed to flash at 95°C, 80°C and 50°C for 10 minutes and condensed product water and remainder brine were analyzed for oil. In addition, experiments were conducted to determine the possible transfer of hydrocarbons from water column in the deaerator system. In this case sequence of experimental conditions of temperature and vacuum were changed i.e. brine was allowed to flash first at 50°C (90 mm Hg) and then at 95°C (630 mm Hg) with only 10 mg/l of oil. Very interesting data were obtained during this experiment. Almost all low boiling n-alkane C₉, C₁₀, and C₁₁ disappeared from both fractions (Figs. 4.2.2-4.2.3). The primary mechanism for this loss from the system is hypothesized to be initial high negative pressure in the system and escape through pump outlet was the possibility. By measuring carbon number concentration in all fractions (viz distillates at 95°C, 80°C and 50°C) including concentrated brine overall carry over of oil was calculated. While doing so essentially a small fraction of oil in the form of UCM might have remained unaccounted which could be safely ignored.

Fig. 4.2.4 shows the presence of n-C₉ to n-C₂₀ in 10 mg/l oil experiment at 95°C (630 mm Hg). In second fraction (80°C) n-C₉ disappeared (Fig.4.2.5). While in third fraction n-C₉ to n-C₁₃ were lost (Fig. 4.2.6) from the distillate. Invariably concentration of all hydrocarbons decreased considerably. In 50 mg/l oil experiment though concentration of n-alkanes decrease in second fraction compared to first fraction but n-C₉ could be detected, however, in third fraction n-C₉ and n-C₁₀ disappeared completely (Fig. 4.2.8-4.2.10). Lowering of concentration was also seen in the concentrated brine (Fig. 4.2.7, 4.2.11).

Similar trend has been found in the experiments of 100 mg/l oil (Figs. 4.2.12-4.2.15). Examination of chromatographic profiles of all figures are self explanatory of hydrocarbon distribution in different fraction at different concentration of oil. As per expectations overall concentration of oil is consistently highest in the first fraction followed by second and third in a given set of experiment. It can be concluded that rates of loss of hydrocarbons from the increasing fractions, and thus the occurrence of chromatographic peaks depend greatly on the negative pressure followed by temperature.

Table 4.2.1 shows transport of oil from concentrated brine to different fractions of distillate at 95°C, 80°C, 50°C and residual oil in a rotating flask. Several variables which can influence the transport of oil have been identified as density, vapour pressure of oil, vapour pressure of water and solubility of oil in water⁵, temperature and vacuum. The vapour pressure of

hydrocarbons with C_8 or more is lower than that of water. Therefore escaping possibility of lower molecular hydrocarbons by condensation is more compared to higher molecular weight. However, this phenomenon is applied in normal distillation/condensation processes. In this experimental set up an additional dragging force in the form of negative pressure was applied in order to flash the brine at a lower temperature. This might have allowed some of the low molecular weight compounds escape without condensation. The average recoveries in case of 10, 50 and 100 mg/l were 21%, 39.4% and 57.2%, respectively (Table 4.2.1).

Table 4.2.1 Transfer of Oil to Distillate (Mass Balance)

oil in Brine	Oil in Fractions			oil in Conc. Brine	Total % Recovery	% loss Escape Sedimentation Adherence etc.
	95°C 630mmHg	80°C 350mmHg	50°C 90mmHg			
mg	mg			mg		
5.01	0.54	0.11	0.03	0.31	20.0	80.0
4.71	0.41	0.12	0.11	0.39	21.9	78.1
4.86(Avg.)	0.48	0.12	0.07	0.35	21.0	79.0
26.02	4.91	3.65	1.70	1.87	46.7	53.3
25.69	3.40	2.69	1.07	1.05	32.0	68.0
25.86(Avg.)	4.16	3.17	1.39	1.46	39.4	60.6
50.64	10.4	10.6	7.55	3.45	63.2	36.8
50.06	11.4	7.26	3.77	3.14	51.2	48.8
50.35(Avg.)	10.9	8.93	5.66	3.30	57.2	42.8
	50°C	95°C				
4.98	2.52	0.85				
5.05	1.57	0.98				
5.02(Avg.)	2.05	0.92				

These data clearly indicate that a large amount of hydrocarbons have been lost during experiments by venting through pump outlet, sedimentation or adherence. As a principle no hydrocarbon or water vapours should have been lost since the latent heat of hydrocarbons above C_8 is much lower than that of water. However, during experiment water droplets were observed in the vacuum tubings though the cooling water temperature was constantly maintained at 10°C . It is thought that some of the hydrocarbon could not be condensed due to vacuum and escaped via vacuum system. This hypothesis was later further strengthened when experiment were done to simulate the deaerator conditions. All hydrocarbons of C_9 - C_{11} boiling range escaped without condensation (Figs. 4.2.2-4.2.3). Furthermore, a dramatic fall in the detector response of other peaks of higher boiling point hydrocarbons was also observed.

Table 4.2.2 shows the normalized transfer rate of oil in 20 ml distillate/10 minutes. It could be seen that highest transfer (0.38) followed by 0.13 and 0.05 mg oil was observed in first, second and third fractions in case of 10 mg/l oil. Similar trends were observed in case of 50 mg/l and 100 mg/l oil concentrations. The values in first and second fractions of 50 mg/l oil were very close which could be attributed to the experimental errors. However, in all cases highest transfer was found in first and lowest in the third fraction of distillate.

To sum up the above, as shown in Table 4.2.2, under the condition that brine flashes, the distillate resulting from the first fraction showed the greatest amount of oil regardless of temperature and pressure. With a high degree of vacuum, the oil amount in the first fraction is particularly high. After the second fraction, the transfer of oil gradually decreases.

Undetected oil (the difference between the amount of oil contained originally in brine and the total of oil contained in evaporated brine and distillate) may be due to the disappearance of the oil to the outside without being condensed (mainly light-gravity oil), adherence on the walls of the equipment or the change of efficiency of extracting organic solvent (methylene chloride) caused by the change of oil quality. Such oil loss decreases as the oil originally contained in brine becomes greater.

As for the composition of oil in distillates and brine after flashing, their Carbon number distribution pattern of oil (the greatest peak at C_{16}). For the first distillate, however, although C_{10} - C_{11} exist in the case of 50°C (high degree of vacuum). For the third distillate, C_9 - C_{13} disappear. C_{11} - C_{13} remain in the post-flashing brine.

Table 4.2.2 Transfer rate of oil(mg) in 20 ml of Distillate/10 min (normalized)

mg oil in Brine	mg oil In Fractions (normalized to 20 ml)			Average % Transfer		
	95°C	80°C	50°C	95°C	80°C	50°C
5.01	0.40	0.15	0.03			
4.71	0.29	0.12	0.08			
4.86(Avg.)	0.38	0.135	0.05	7.81	2.78	1.02
26.02	2.98	3.40	1.51			
25.69	2.89	2.44	0.95			
25.86(Avg.)	2.93	2.94	1.23	11.3	11.3	4.75
50.64	10.1	10.3	6.04			
50.06	11.4	7.85	3.77			
50.35(Avg.)	10.8	9.07	4.90	21.35	18.01	9.73
	50°C	95°C		50°C	95°C	
4.98	2.46	0.87				
5.05	1.37	1.15				
5.02 (Avg.)	1.92	1.01		38.2	20.1	

5. Conclusion

- (1) The initial observations lead to several conclusions concerning the transport behavior of oil from brine to distillate at different temperatures, pressures and oil concentrations. First, the greatest transport of oil was observed in the first fraction of distillate collected at high temperature and low pressure (95°C, 630mm Hg) and the lowest transport was at low temperature and high vacuum (50°C, 90mm Hg). Secondly, the highest transfer of oil was also found in the first fraction of distillate when conditions were simulated to deaerator conditions i.e., 50°C, 90mm Hg followed by second fraction (95°C, 630mm Hg). It could be hypothesized that whether brine boiled at high temperature (100°C, 760 mmHg) or flashed at high negative pressure (22°C, 20mm Hg) the transport of oil will occur maximum in the first fraction of distillate. Thirdly the oil transport was found to be directly proportional to the concentration of oil present in the brine. The % total recovery of oil was also increased with the increasing concentration.
- (2) Capillary gas chromatographic/mass spectrometry method for the determination of oil was found to be superior to infrared spectroscopy because of individual compounds identification and use of relatively less toxic extraction solvents. Total organic carbon analysis method appears to be inefficient for the analysis of undissolved portion of oil.

6. Recommendation for Future Work

- (1) In order to obtain meaningful data to be able to quantitatively evaluate transport of oil into product water in desalination plants, highly simulated MSF test plant will be required.
- (2) More experiments with lower concentrations (1-5 mg/l) of oil and varying conditions of temperature and vacuum should be planned.

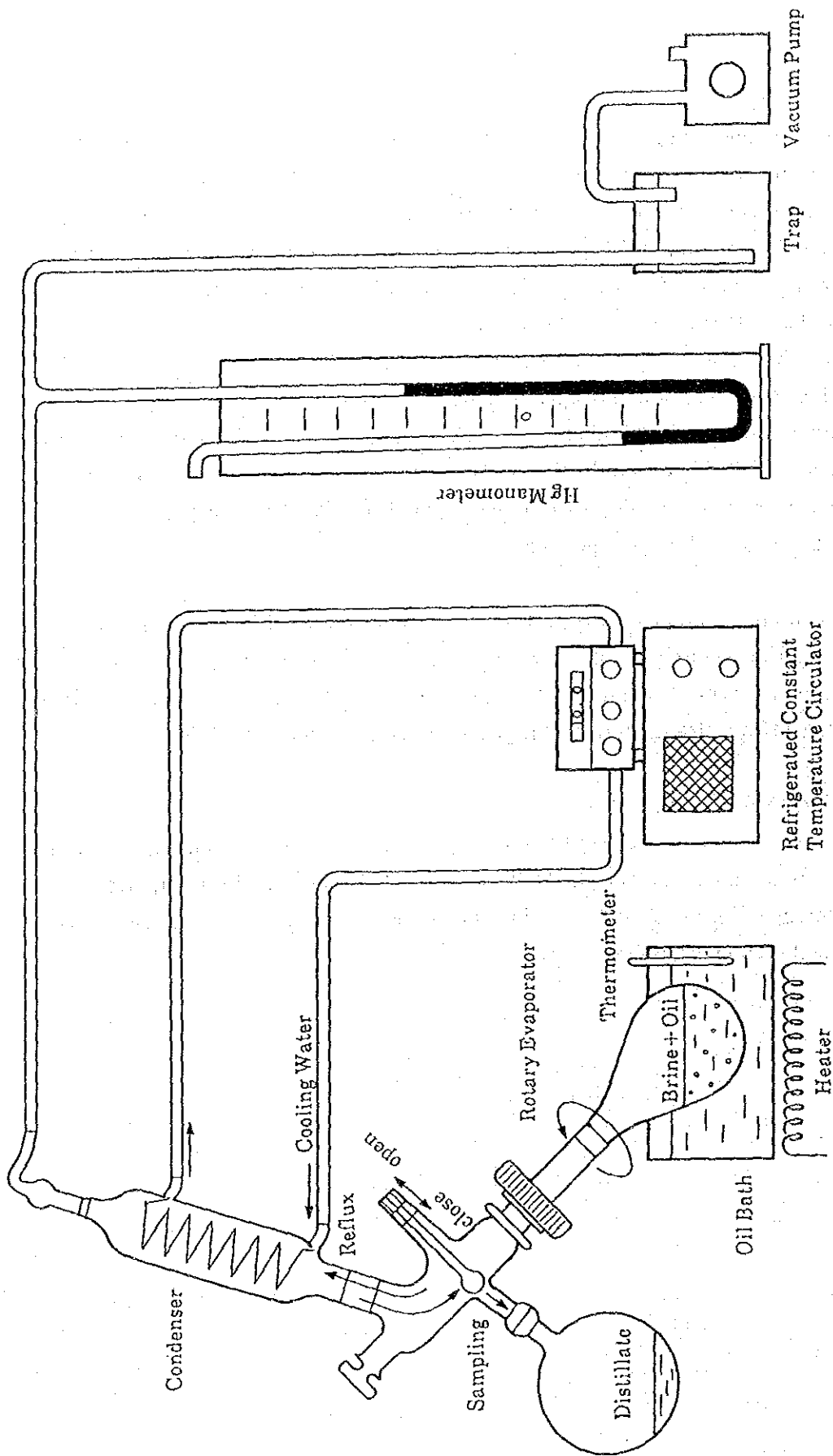


Fig.3.1.1 Schematic Diagram of Oil Carryover Test Unit

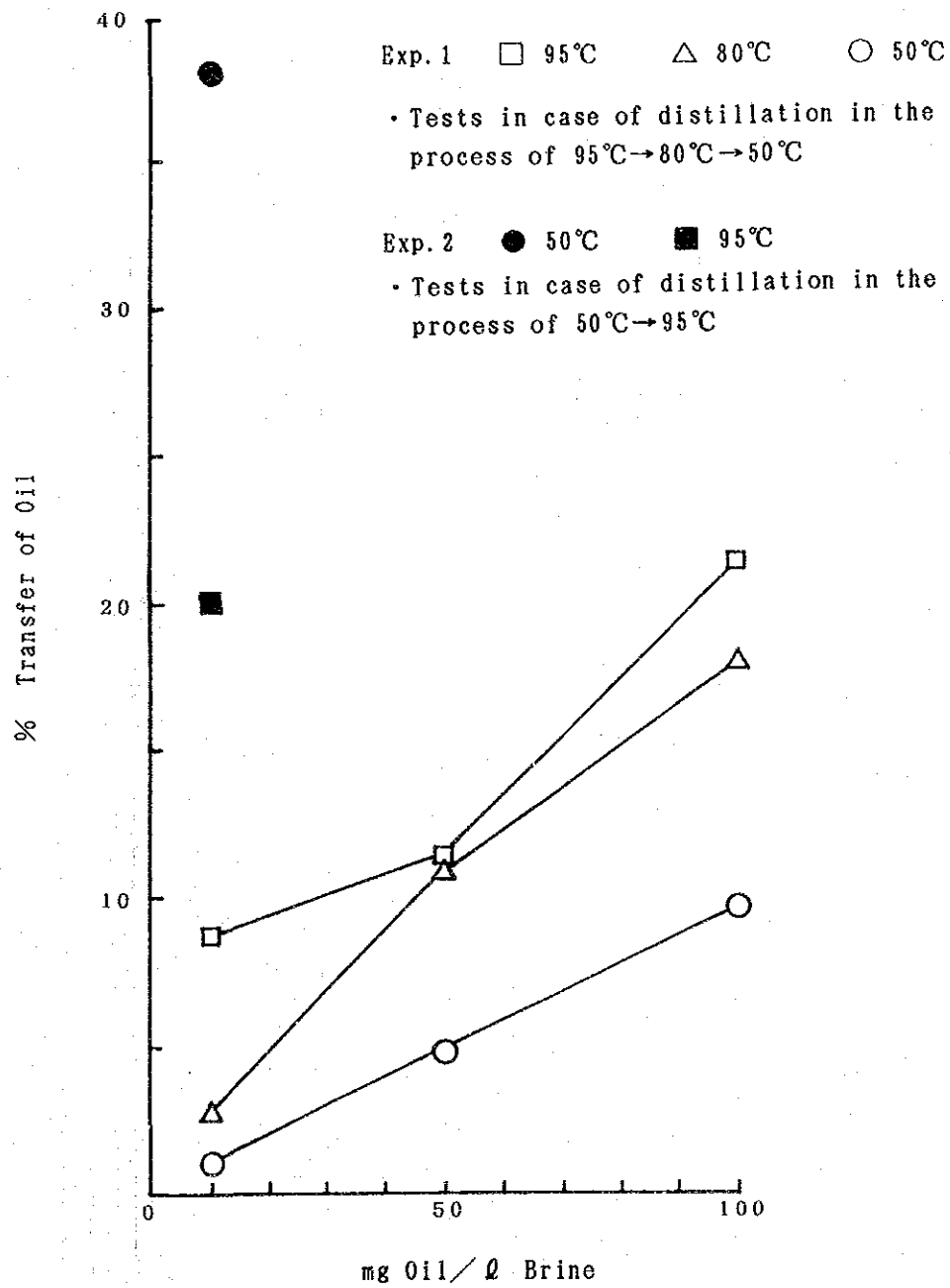


Fig.4.1.1 Average transfer of oil at different temperatures

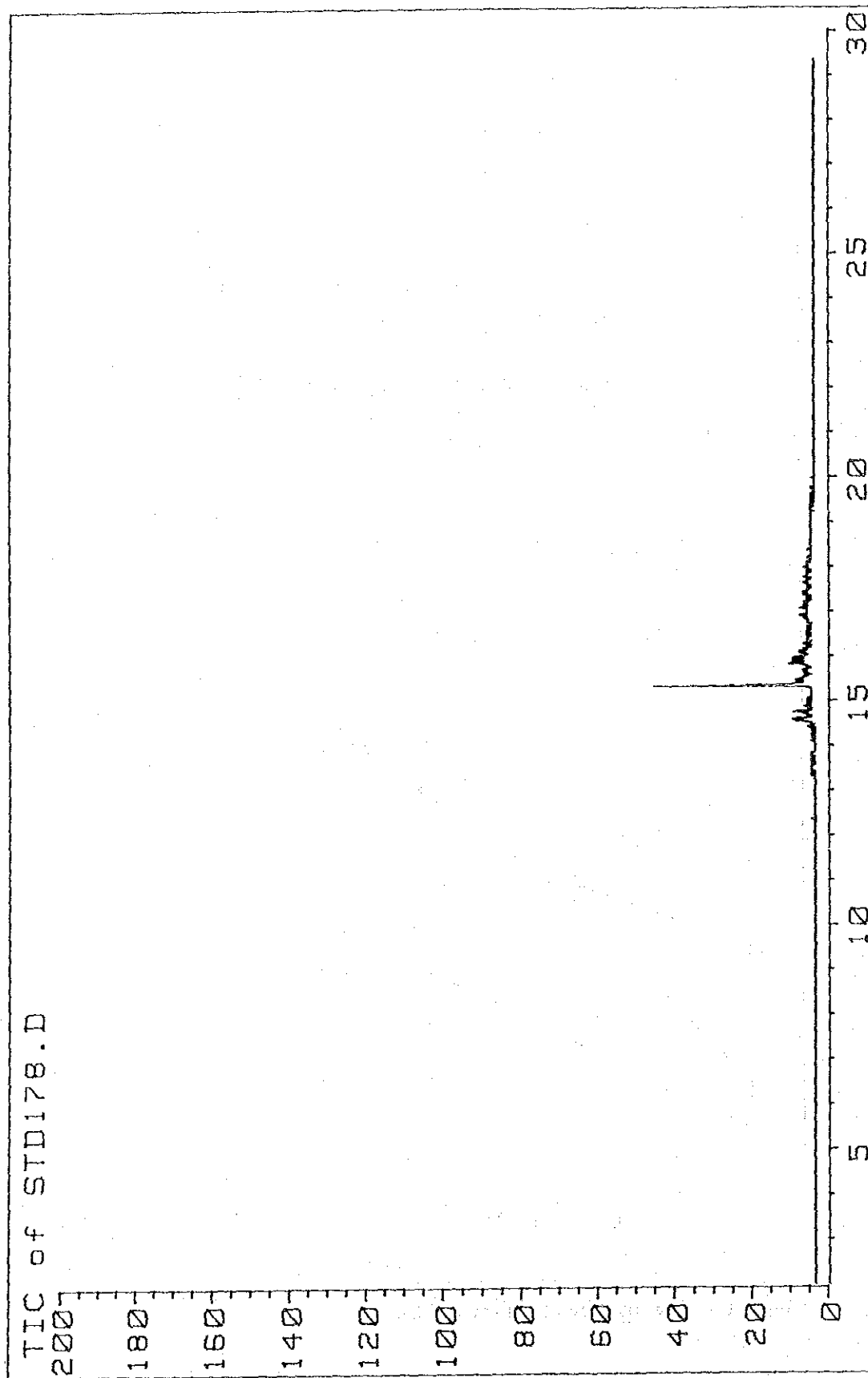


Fig.4.1.2 Computer reconstructed ion chromatogram of diesel fuel oil in selected ion monitoring of m/z 178 for polycyclic aromatic hydrocarbons

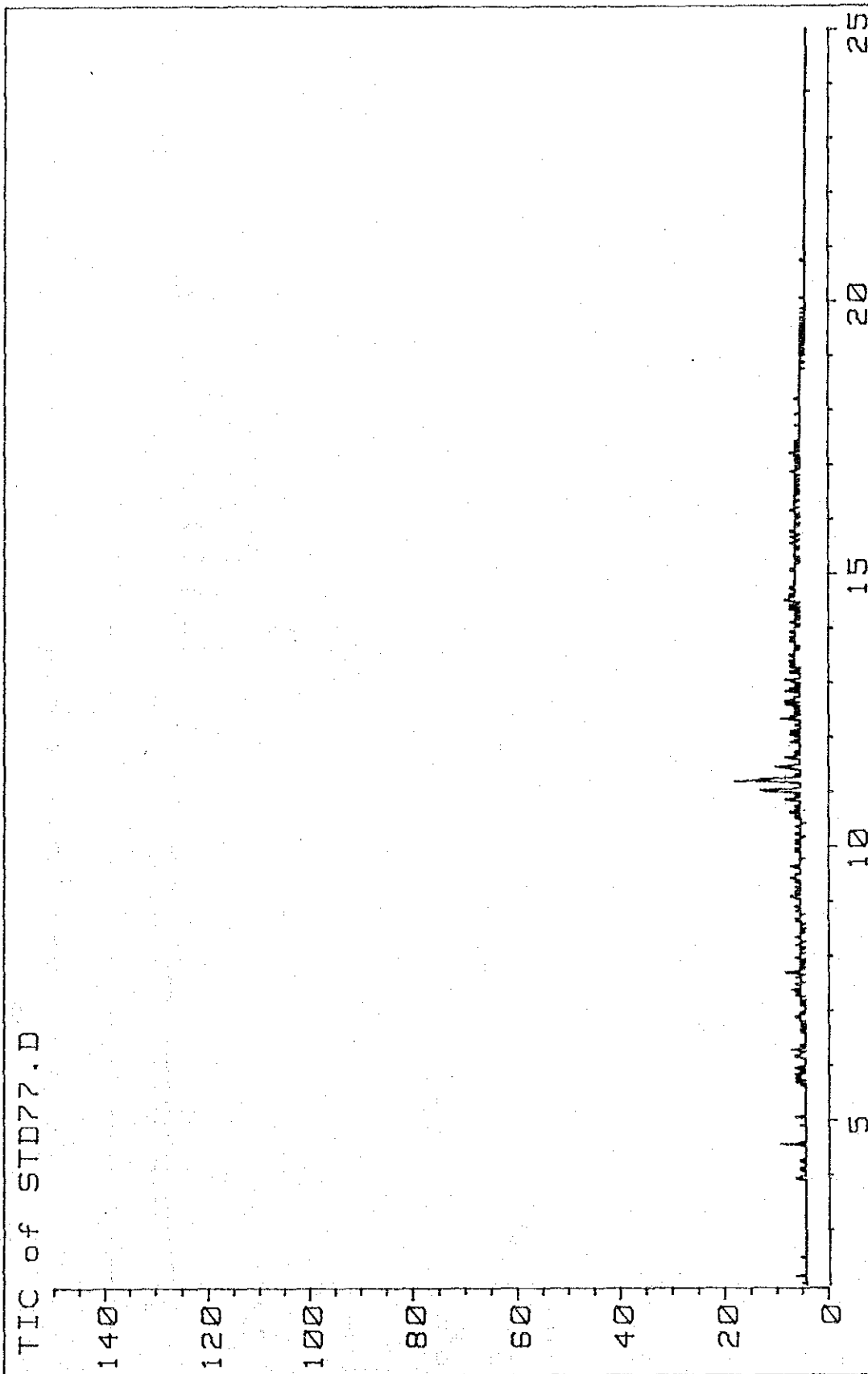


Fig.4.1.3 Computer reconstructed ion chromatogram of diesel fuel oil in selected ion monitoring of m/z 77 for substituted phenyls

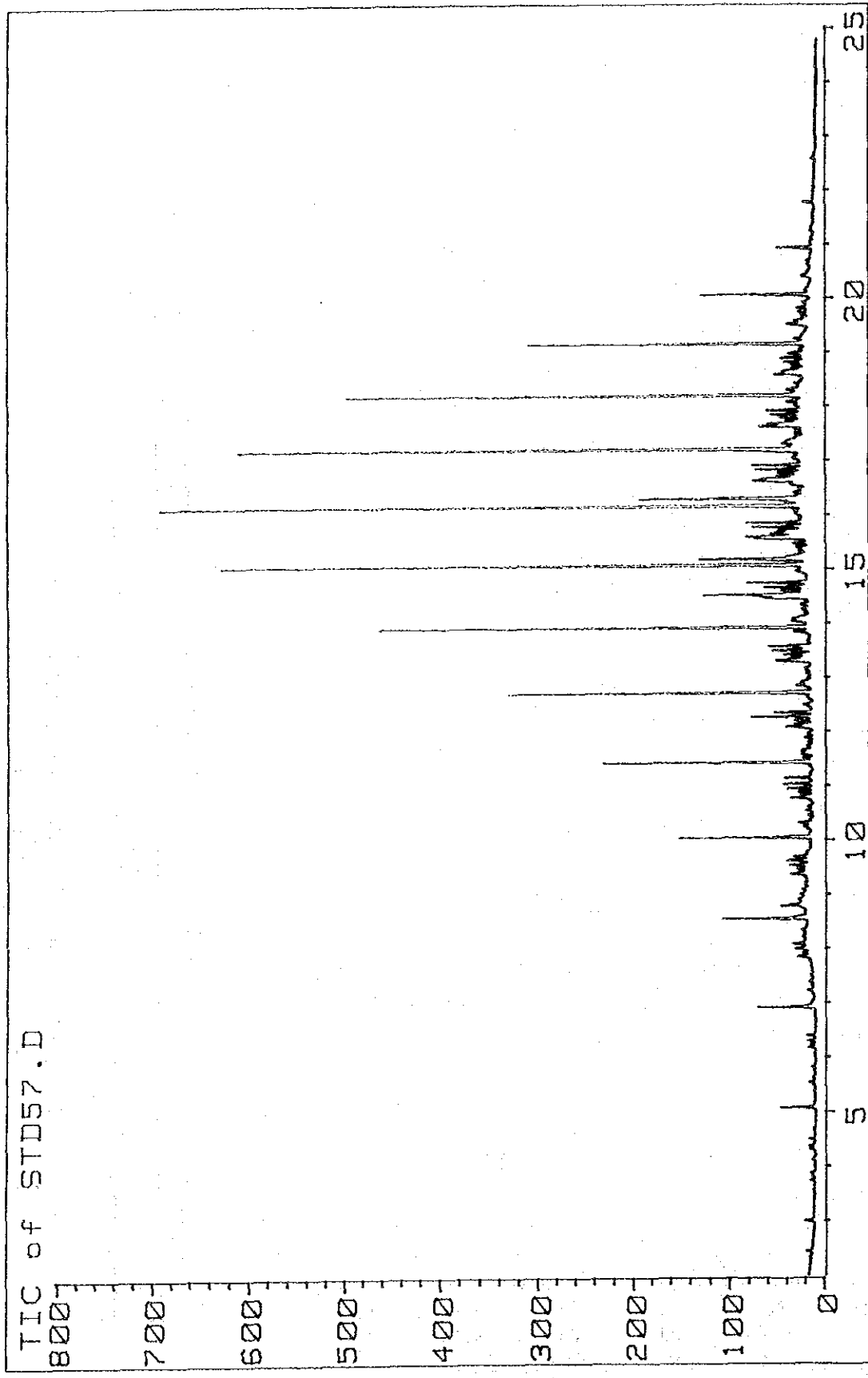


Fig.4.1.4 Computer reconstructed ion chromatogram of diesel fuel oil in selected ion monitoring of m/z 57

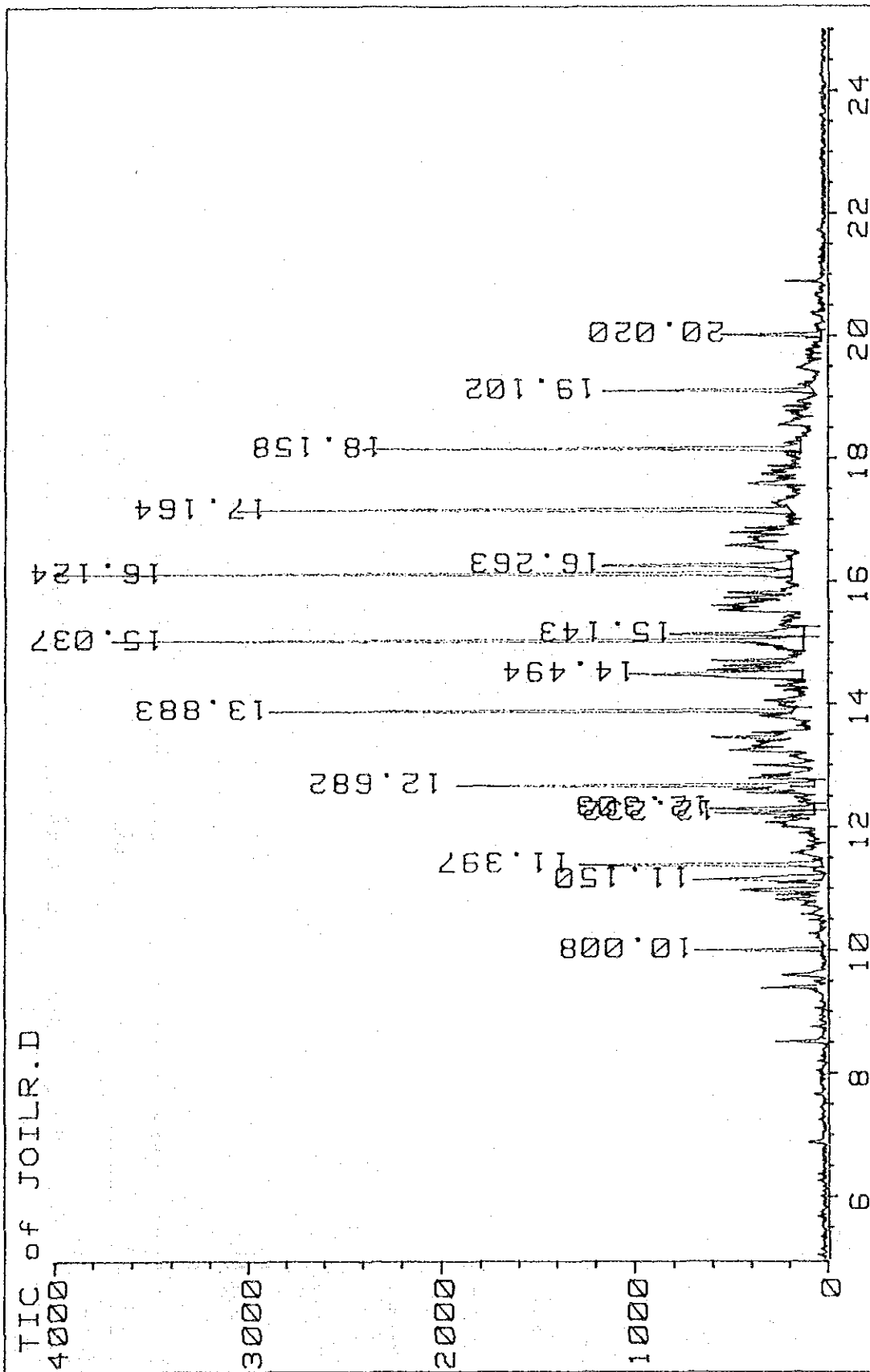


Fig.4.1.5 Computer reconstructed ion chromatogram of diesel fuel oil in scan mode monitoring of m/z 150-500

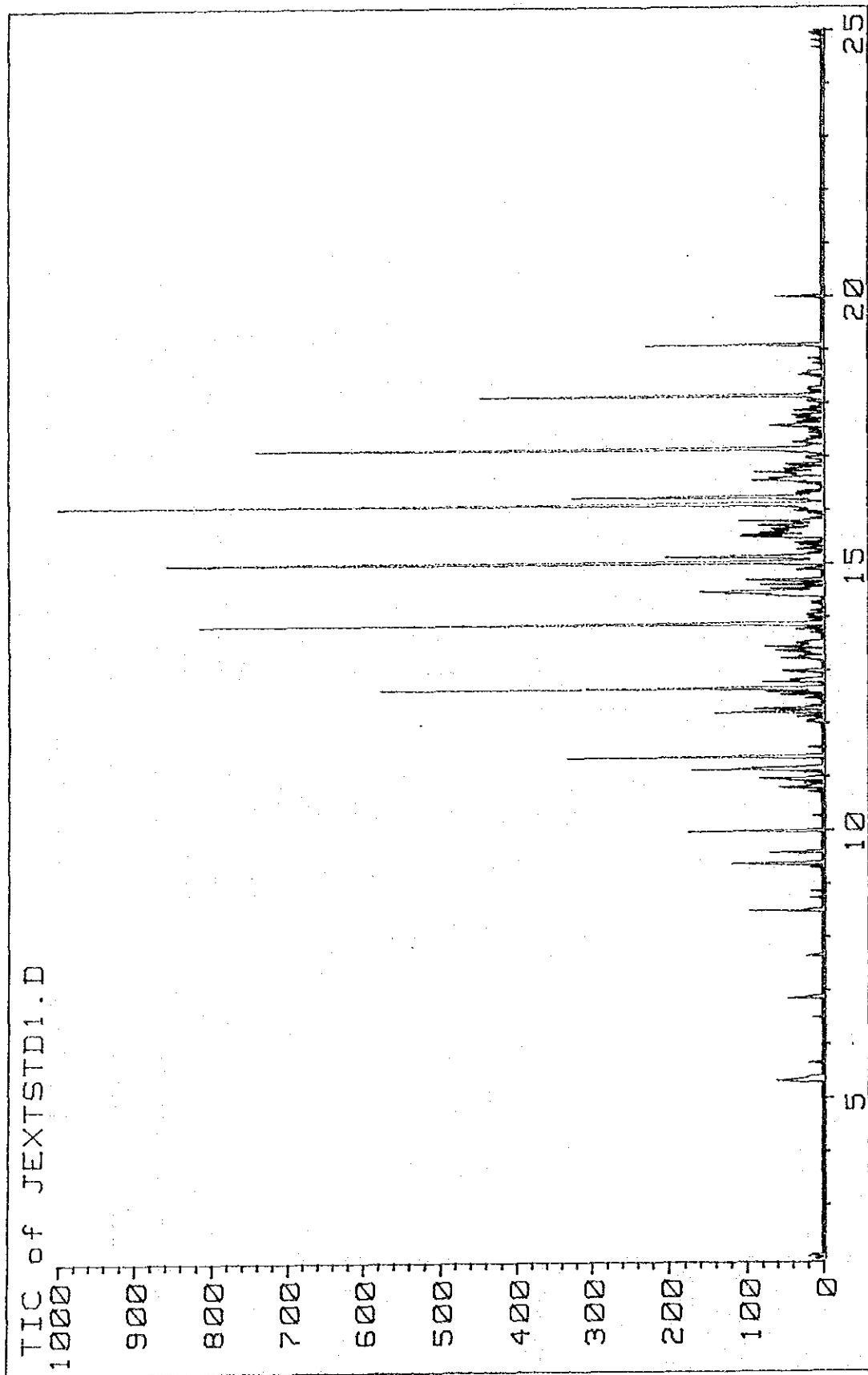
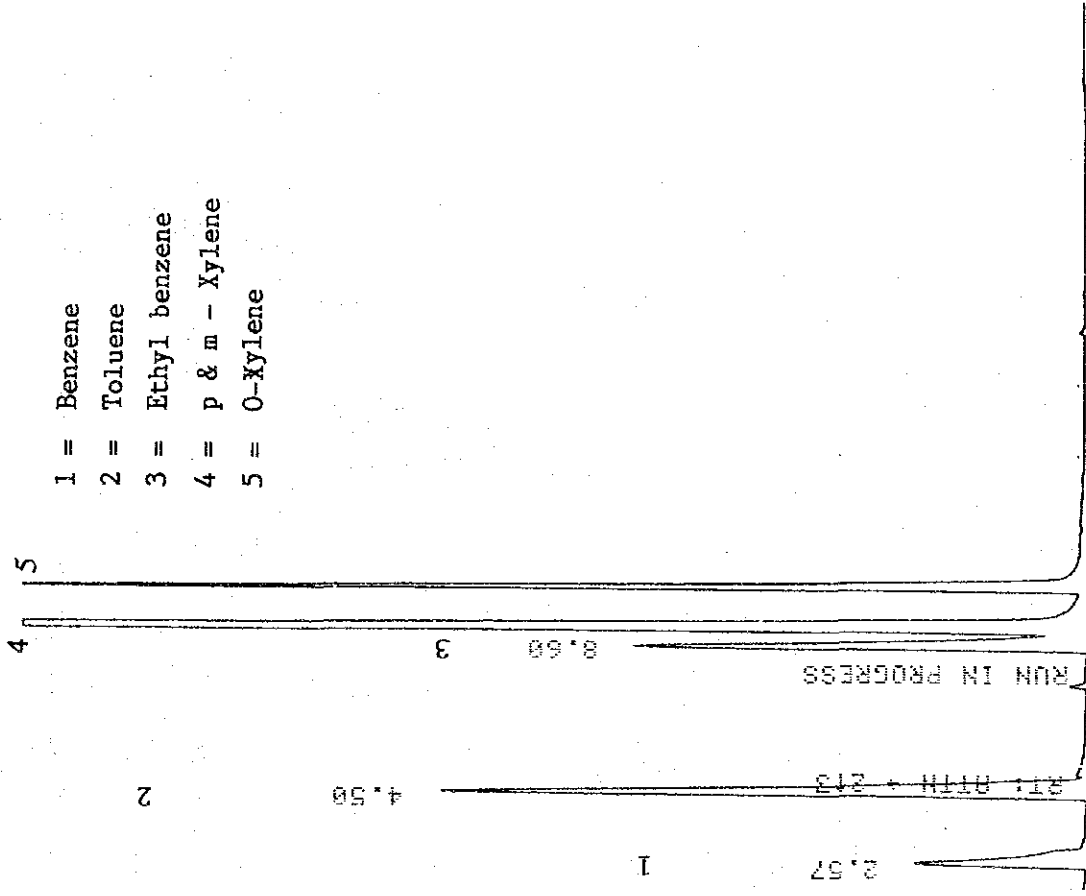


Fig.4.1.6 Computer reconstructed ion chromatogram of water extracted oil in scan mode

10.00
10.10
10.20



- 1 = Benzene
- 2 = Toluene
- 3 = Ethyl benzene
- 4 = p & m - Xylene
- 5 = O-Xylene

Fig.4.2.1 Gas chromatogram of water soluble aromatic hydrocarbons(BTEX) by purge and trap device

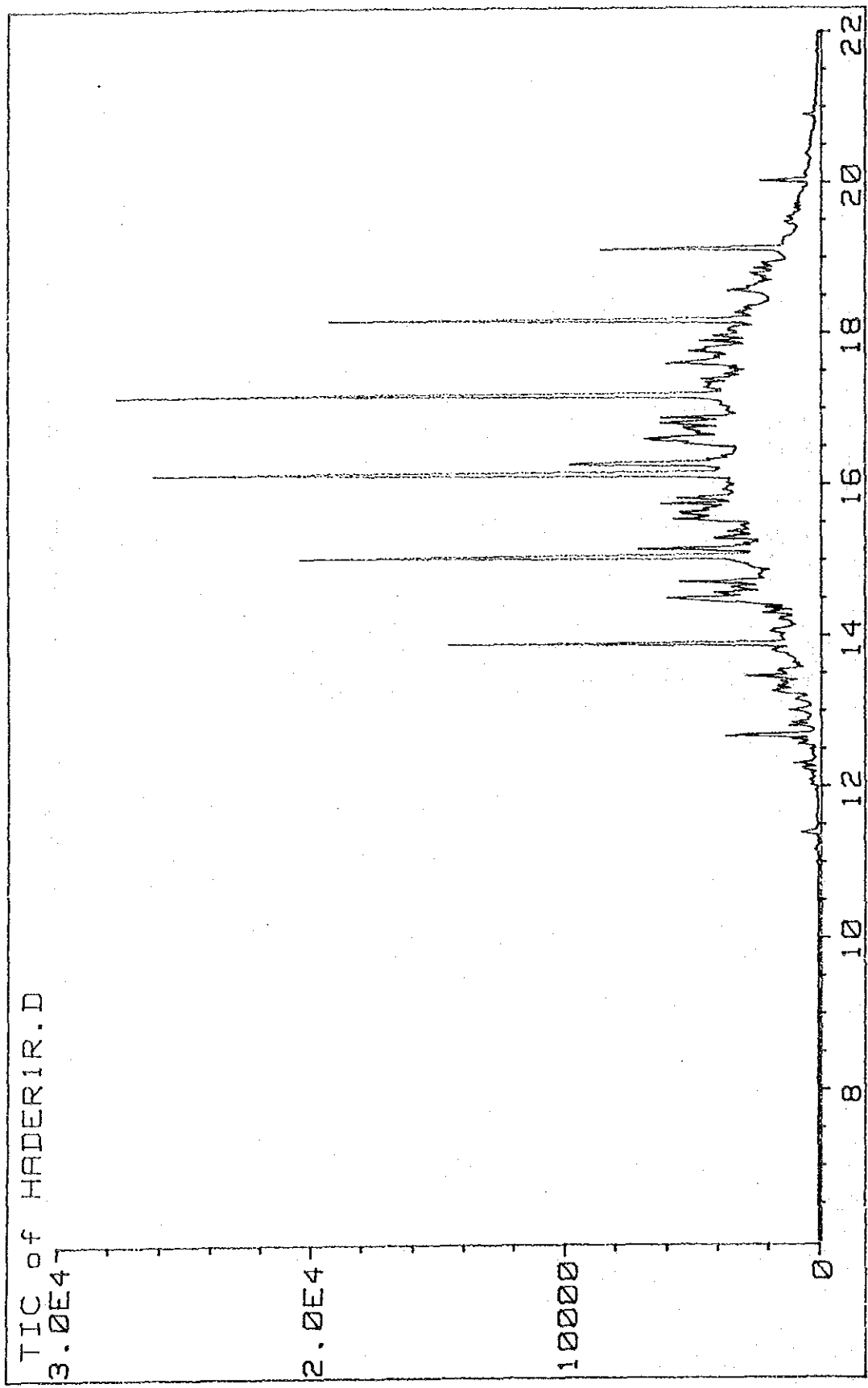
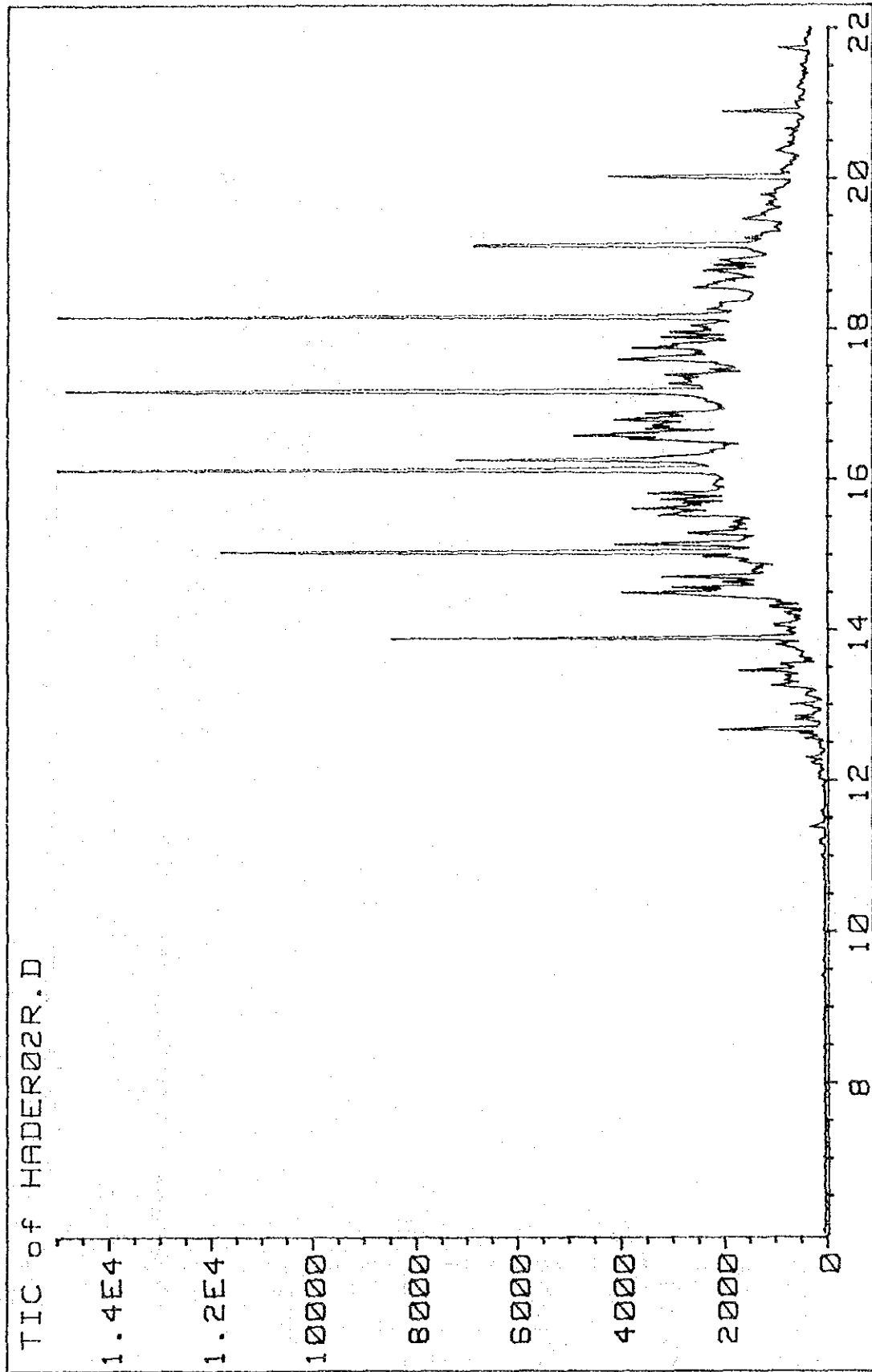


Fig.4.2.2 Computer reconstructed ion chromatogram of first fraction of deaerator simulated test



3.2.23

Fig.4.2.3 Computer reconstructed ion chromatogram of second fraction of deaerator simulated test