Sea water 600 ml + Fuel oil A 3 ml / 1 l beaker

↓

Ultrasonic treatment (ultrasonic cleaner) 15 min

↓

Leave to stand 10 min

↓

Collect 350 ml from the bottom of the container

↓ ← **Sea water**

Dilute (x 1, 3, 10, 30)

↓

Measure oil content (TOC method, Fluorophotometry)

Fig. 16 Method of determining the oil content in sea water containing dispersed oil by the TOC method and by fluorophotometry

<u>Measurement conditions</u>

Slit width	:	excitation 10 nm, fluorescence 10 nm
Excitation wavelength	:	310 nm
Fluorescence wavelength	:	343 nm

(3) Results and Discussion

(3)–1 Determination of optimum excitation and fluorescence wavelengths

The results of scanning excitation and fluorescence wavelengths show that, for fuel oil A, the optimum wavelengths are:

Excitation wavelength	:	310 nm
Fluorescence wavelength	:	343 nm

(See Fig. 17)

However, since the blank isooctane also has peaks at the optimum excitation and fluorescence wavelengths of 310 nm and 343 nm, compensation for the blank is essential (Figure 18).

(8.1.2.A)

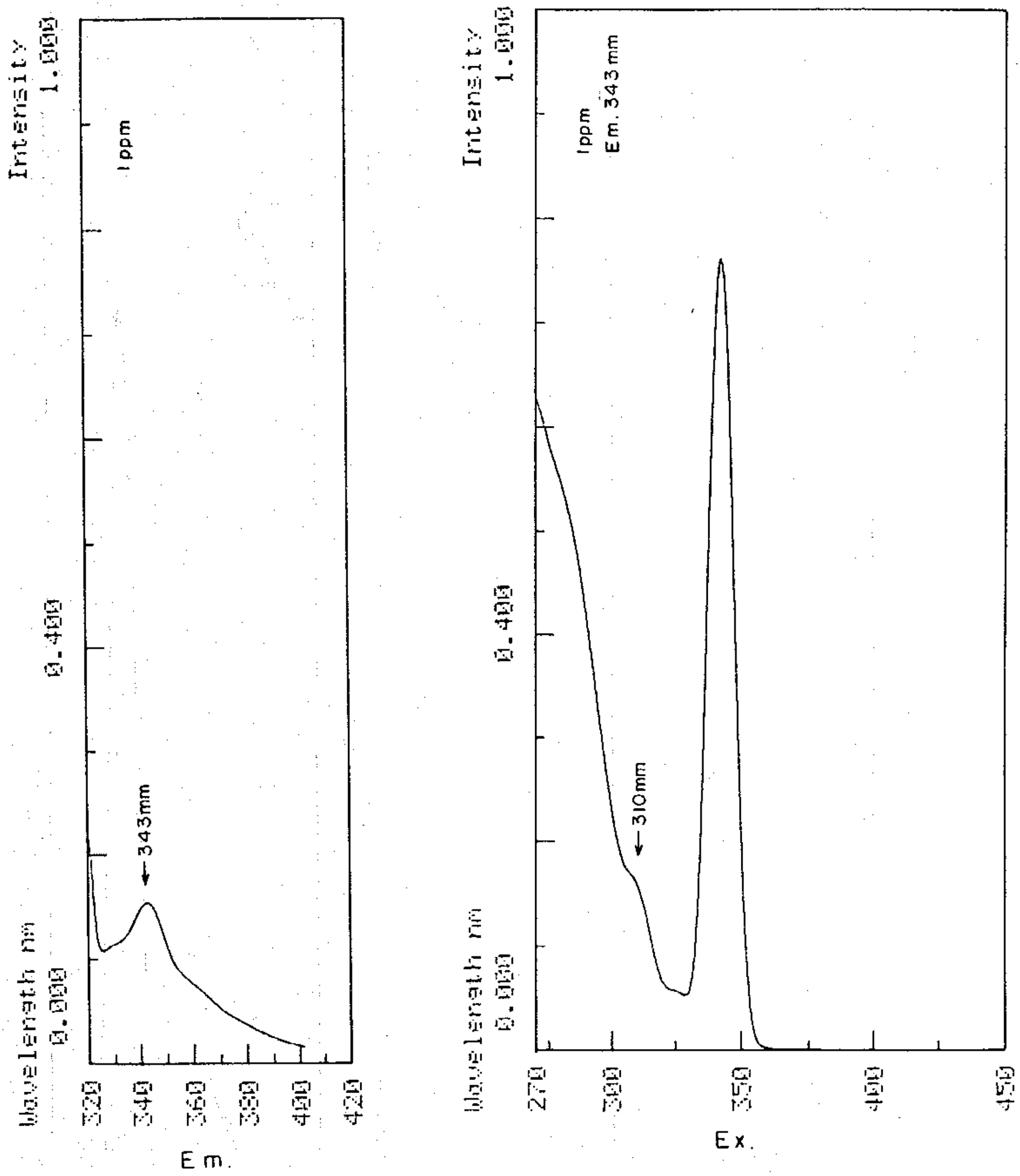


Fig. 17 Scanning for Fuel Oil Type A (1ppm/ isooctane)

(8.1.2.A)

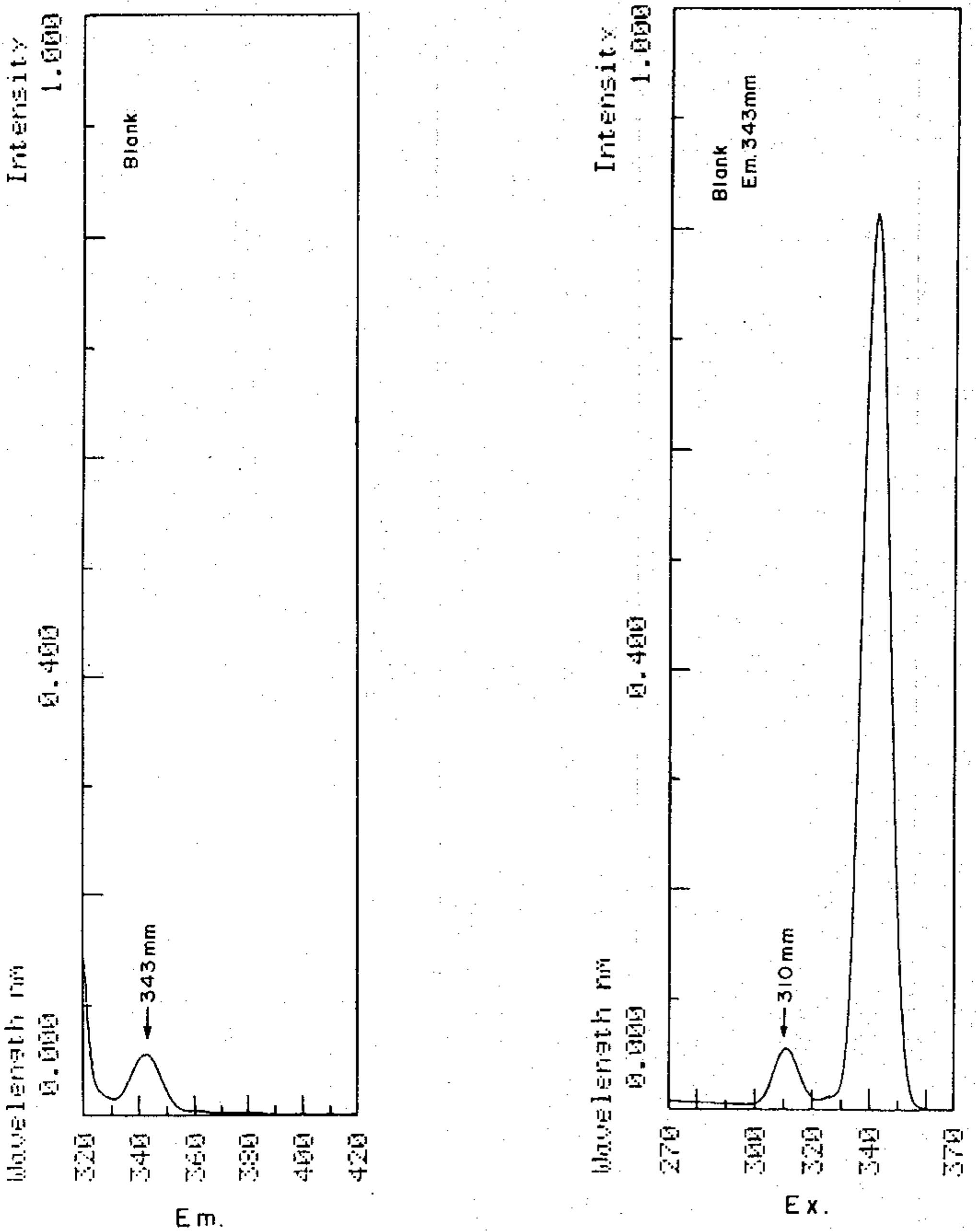


Fig. 18 Scanning for isooctane

(3)-2 Experimental Results

The resulting calibration curves are shown in Figs. 19 ~ 25.

(1) Range of concentrations susceptible to measurement

In the case of Fuel oil Type A, the measurability of concentrations of the order of 10 ppb to 50 ppm was confirmed.

For concentrations less than about 10 ppb, although detection as fluorescent intensity is possible, there are large errors which do not fall on a straight line (See Figs. 1.19 ~ 24. We also confirmed that concentrations over about 50 ppm plot off the straight line and the bias tends to reach a peak (See Fig. 25.

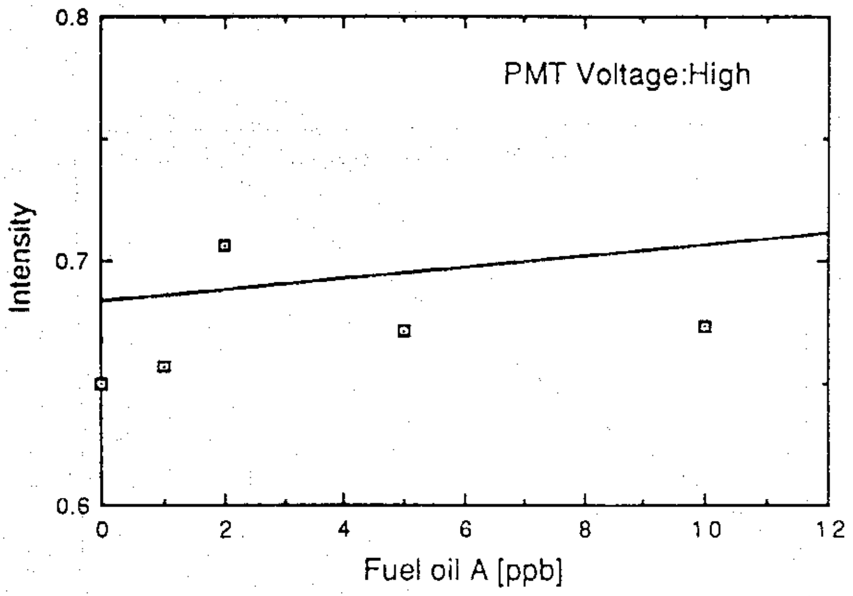


Fig. 19 Fuel oil A fluorophotometry calibration curve (1)

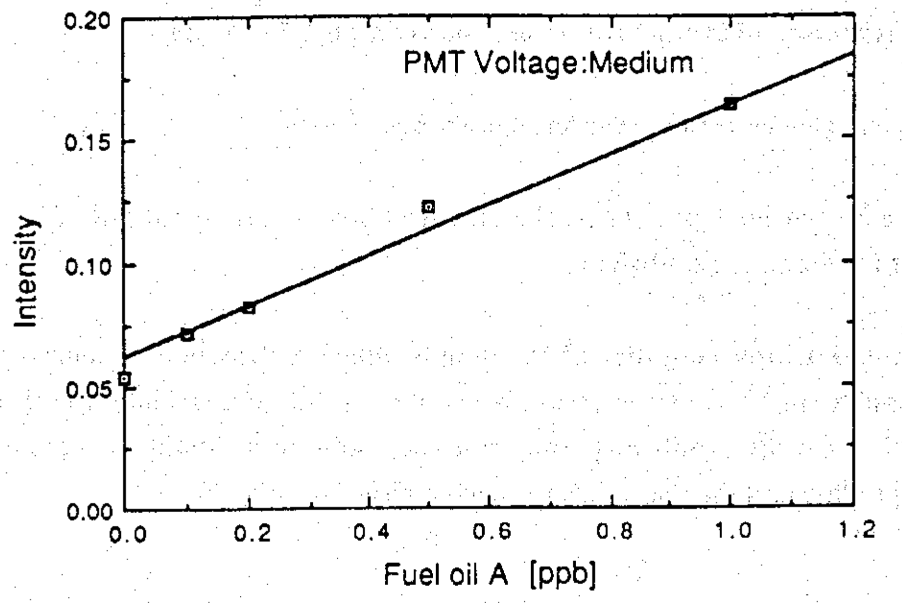


Fig. 20 Fuel Oil Type A Fluorophotometry Calibration Curve(2)

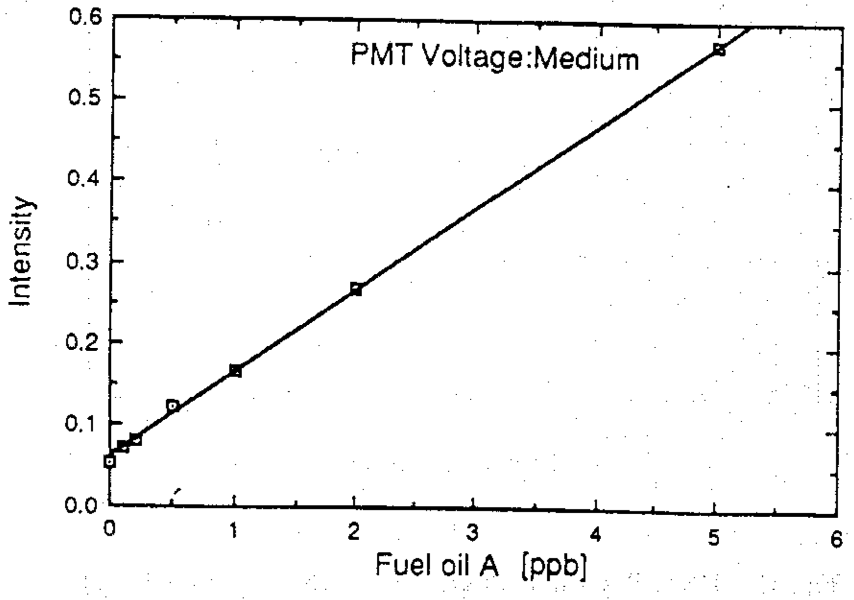


Fig. 21 Fuel Oil Type A Fluorophotometry Calibration Curve(3)

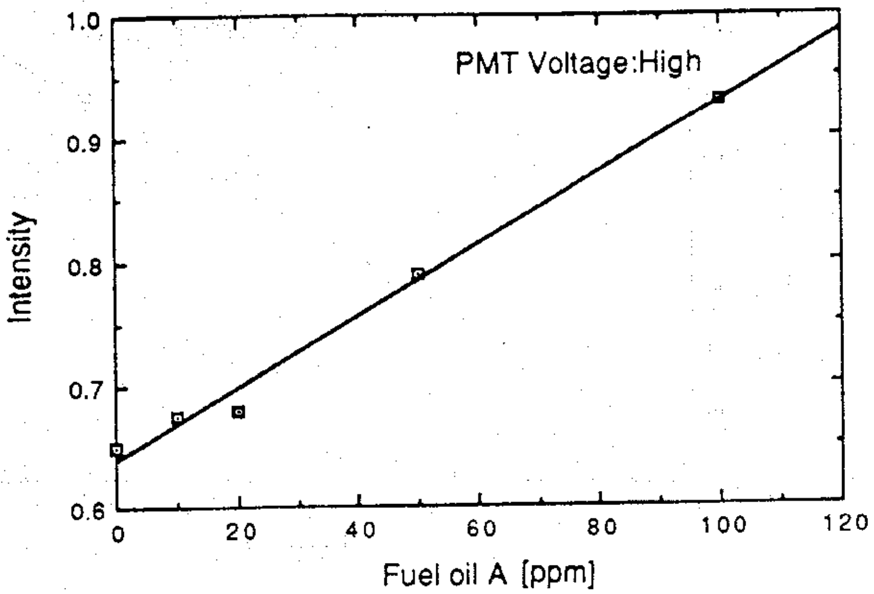


Fig. 22 Fuel Oil Type A Fluorophotometry Calibration Curve(4)

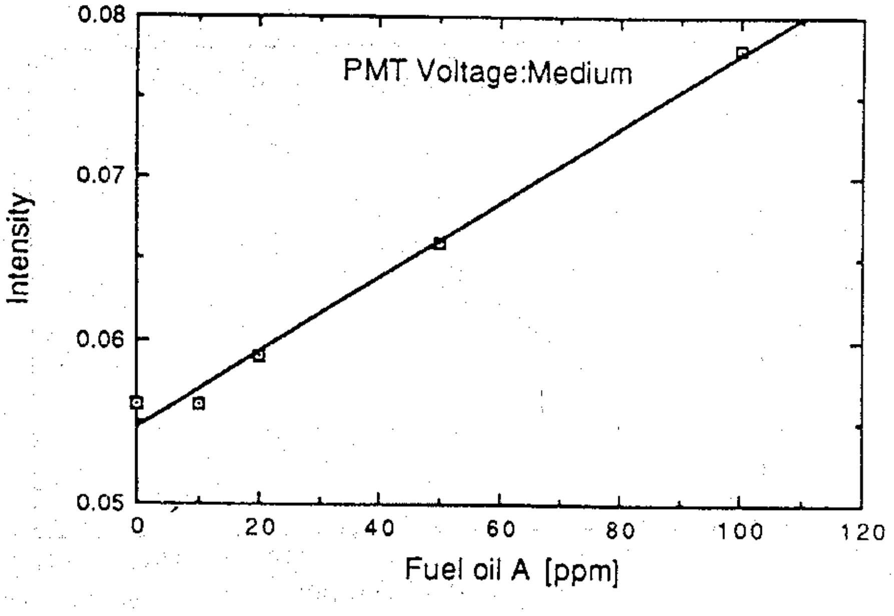


Fig. 23 Fuel Oil Type A Fluorophotometry Calibration Curve(5)

(8.1.2.A)

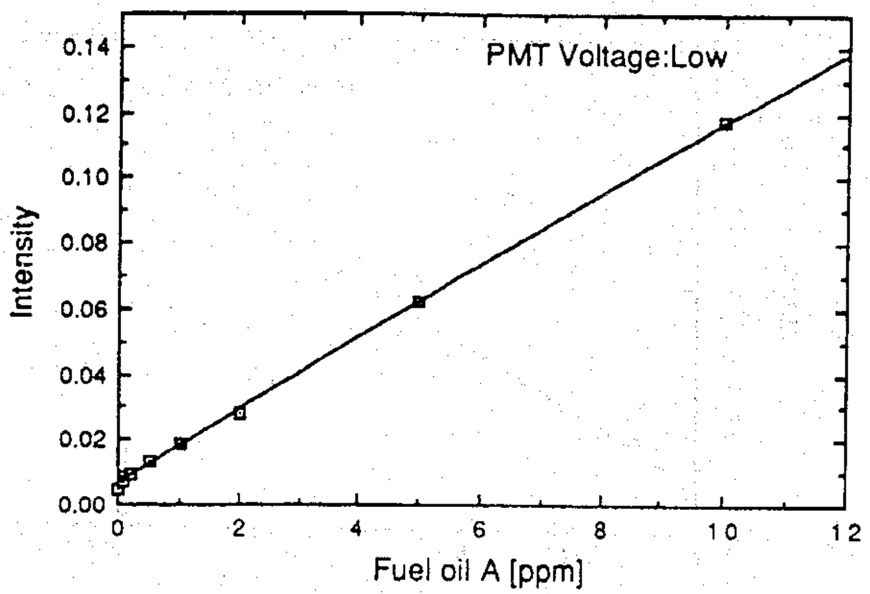


Fig. 24 Fuel Oil Type A Fluorophotometry Calibration Curve(6)

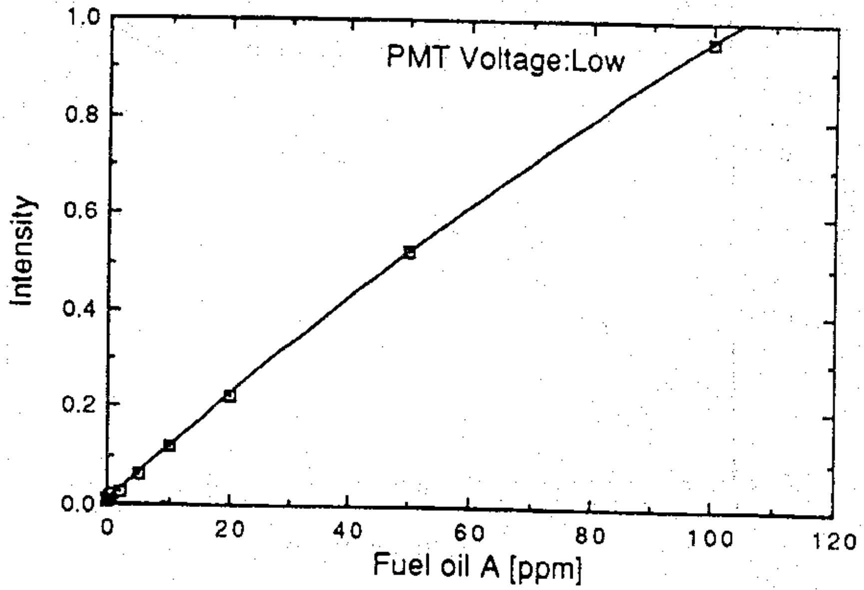


Fig. 25 Fuel Oil Type A Fluorophotometry Calibration Curve(7)

(3)-3 Study of extraction method with actual samples

1) Study of quantity of isooctane used for extraction (Table 3)

The more isooctane used for extraction, the higher the test material extraction efficiency. However, too much extraction solvent could be considered inconvenient to handle.

Bearing in mind that the extraction efficiency is not ideal, here we have decided to use 10 ml in future.

Table 3 Quantity of added isooctane and oil content extraction rate

Added isooctane [ml]	Fluorescent[*1.3.1] intensity	Oil content[*1.3.2] [ppm]	Extraction[*1.3.3] rate [%]
5	0.147	0.69	49
10	0.185	1.03	74
20	0.219	1.40	100

*1.3.1 : Readings with medium voltage

*1.3.2 : Fuel oil A calibration curves were used to convert fluorescent intensity readings to oil content values (after compensation for the blank in the sea water).

*1.3.3 : The oil content extracted with 20 ml of added isooctane was made 100%.

2) Repetitive extraction study (Table 4)

Almost all the oil content was collected in the first extraction operation. Subsequent extraction operations collected hardly any oil and the oil content extracted in the third operation was undetectable.

From these results, and in view of the trouble involved in the operation, it can be considered that the first of the repetitive extractions is adequate.

Table 4 Repetitive extraction and oil content detection (Extraction isooctane quantity = 10 ml)

Repetitive extraction number	Fluorescent intensity[*1.4.1]	Oil content [ppm][*1.4.2]
1	0.180	0.97
2	0.085	0.02
3	0.078	0

*1.4.1 : Readings with medium voltage

*1.4.2 : Fuel oil A calibration curves were used to convert fluorescent intensity readings to oil content values (after compensation for the blank in the sea water).

3) Study of the necessity for cleaning the inner wall of the separating funnel after collecting the isooctane layer (Table 5).

Almost all the oil content was collected in the first extraction operation. After the test material had been collected, no oil could be detected in the washings from the inner wall of the separating funnel.

Consequently, we can say that there is no necessity to wash the inner wall of the separating funnel after the isooctane layer has been collected.

Table 5 Study of the necessity to wash the inner wall of the separating funnel after collecting the isooctane layer

(Extraction isooctane quantity – 10ml)

	Fluorescent intensity[*1.5.1]	Oil content[*1.5.2] [ppm]
First extraction test material	0.172	0.89
Inner wall washing test material	0.077	0

*1.5.1 : Readings with medium voltage

*1.5.2 : Fuel oil A calibration curves were used to convert fluorescent intensity readings to oil content values (after compensation for the blank in the sea water).

(3)–4 Experimental Results

We extracted sea water with isooctane and compared the patterns obtained on scanning the excitation and fluorescence wavelengths and the fluorescent intensity measurements under the same conditions with those for isooctane. The results confirmed that, although the quantity was minute, material which produced fluorescence was also present in the sea water.

Consequently, when measuring sea water containing dispersed oil, a blank compensation is necessary.

It is possible that these fluorescence producing materials in sea water are amino acids.

Table 6 Results of measuring fluorescent materials in sea water

Impressed voltage	Fluorescent intensity	Fuel oil A concentration conversion*1.6.1
High	0.976	116ppb
Medium	0.081	170ppb
Low	0.008	0.2ppm

*1.6.1 : Fuel oil A calibration curves were used to convert fluorescent intensity readings to oil content values (after compensation for the blank in the sea water).

(3)–5 Reproduction check

The results of repeated reproduction investigations with the same sample confirm that reproducibility is excellent and the method of measurement is highly reliable.

Table 7 Results of fluorophotometry measurements of the oil content in sea water containing dispersed oil

Measurement number	Fluorescent intensity*1.7.1	Oil content [ppm]*1.7.2
1	0.169	0.86
2	0.170	0.87
3	0.171	0.87
4	0.173	0.89
5	0.172	0.88
Average	0.171	0.87
SD	0.002	0.01

*1.7.1 : Readings with medium voltage

*1.7.2 : Fuel oil A calibration curves were used to convert fluorescent intensity readings to oil content values (after compensation for the blank in the sea water).

(3)–6 Experimental Results

In this experiment, in respect of test material with oil contents up to 7.5 ppm, there was a linear relationship between the fluorophotometry and the corresponding average measurements by the TOC method, the correlation being:

TOC Method / fluorophotometry ≒ 0.6

(However, the values measured by the TOC method showed a scatter of 1.1 to 3.1 ppm.)

In test material with an oil concentration of 25 ppm, as determined by fluorophotometry, the average of the values measured by the TOC method was 8.3 ppm, which is a widely different ratio of 0.3 (See Fig. 26, Table 8)

The reason for this is thought to be as follows. With high oil concentrations, even if the oil droplets in the test material are microscopic and float up extremely slowly, as they collide with each other they grow larger and float up to the surface of the test material with increasing speed. Since these surface can be captured by the TOC method, which measures the oil content within the test material, the ratio of oil content measurements obtained by the TOC method to oil content measurements obtained fluorophotometry is less than for test materials with lower oil concentrations.

Since the quantity of test material used for one measurement with the TOC method is only several tens of microliters, errors can arise readily because of the small number of oil droplets which can be captured, particularly when the oil concentration in the test material is low. Conversely, when the oil concentration is high, one can believe that part of the oil content in the test material floats out to the surface and escapes capture by the TOC method. So, it is understandable that measured values will be less than the true oil content.

In the case of the fluorophotometric method, a major disadvantage is the time and trouble involved compared to the TOC method, which means that large quantities of test materials can not be tested in a limited time.

However, the quantity of test material used for the measurement is much greater than that required for the TOC method and, since the measurements are made after extracting the oil content, the above mentioned disadvantages of the TOC method are avoided and the results are extremely reliable, as shown in Table 7 of this report,

Consequently, in order to obtain highly reliable results, we believe the usage of fluorophotometry is preferable to the TOC method.

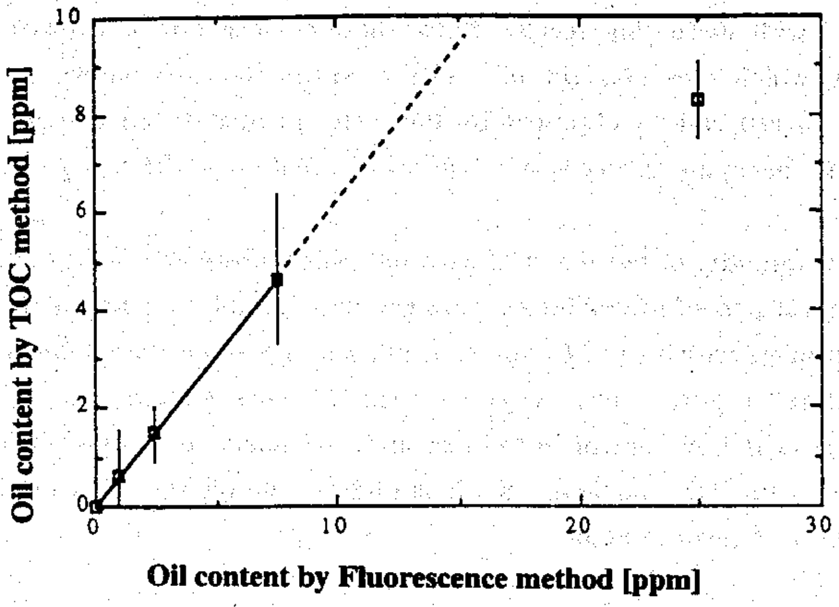


Fig. 26 Oil content of oil–sea water dispersions at various concentrations by the fluorescence and TOC methods

Table 8 Measurement of oil content in oil–sea water dispersions at various concentrations

Oil–sea water dispersion	Oil content [ppm]		TOC/Fluorescence*1.8.1
	Fluorescence method	TOC method*1.8.1	
x 1 (undiluted)	25	8.3	0.3
diluted x 3	7.5	4.6	0.6
diluted x 10	2.4	1.5	0.6
diluted x 30	0.9	0.6	0.7

*1.8.1 : TOC values are averages of three measurements for each sample

(4) Conclusion

- **Concentration is supported from about 10 ppb to 50 ppm.**
- **Extraction conditions for oil–sea water dispersions have been established. Reproducibility of the measured values is extraordinarily good.**
- **Since a certain amount of fluorescent material is present in sea water, compensation is needed in the case of test material measurements.**
- **There is a correlation with the TOC method if the oil content concentration in the oil–sea water dispersion is low but this correlation disappears when the concentration exceeds a certain limit.**

The results of studying this method show that, when using fuel oil A, it is feasible from 10 ppb to 50 ppm where the reproducibility is high and the background is low. Also, the amount of sample required is comparatively small at 50 ml.

Since the aromatic ring content varies according to type of oil used, this has a bearing on the sensitivity of the measurements according to the oil type but, if the oil type is constant, this is not a problem.

2. Comparison of various measurement methods

The results of studying various methods of measurement are shown below:

Correlation

IR (simple oil content meter)/TOC method : Approx 1.5 (TOC oil content studied between 25 and 560 ppm)
IR (JIS method)/TOC method : Approx 1.8 (TOC oil content studied between 3 and 9 ppm)
GC/TOC Method : No correlation (TOC oil content studied between 1 and 13 ppm)
Fluorescence/TOC method : Approx 1.6 (TOC oil content studied between 1 and 5 ppm)

Measurement ranges

IR (simple oil content meter) : 0.25 ppm to ... (published data)
IR (JIS method) : 1 ppm (with 1 litre of sample) to ...

TOC : 100 ppb to ... (smallest graduation on SWCC TOC meter)
Gas chromatography : 5 ppm (with 1 liter of sample) to ...
Fluorophotometry : 10 ppb to 50 ppm

- **IR data are derived from a literature search.**
- **Actually, lack of good quality carbon tetrachloride at SWCC makes IR applications difficult.**

The various methods of oil content measurement are summarized in Table 9. For actual measurements, the TOC method was used for beaker scale experiments where large quantities of samples were not available. Fluorophotometry was applied in other cases.

Table 9 Comparison of various oil content measurement methods

Method	Advantages	Disadvantages	General appraisal of implementation at SWCC *
n-hexane (Mass method)	·Universal ·Established technology	·Low sensitivity ·Long measuring time (several tens of minutes per sample) ·Low boiling points oils evaporate	x
Carbon tetrachloride extraction (IR method)	·Universal ·Established technology	·Large samples needed (1 liter for 1 ppm) ·Lack of good carbon tetrachloride at SWCC gave high background ·Long measuring time (several tens of minutes per sample)	x
Simple oil content	·Quick (5 minutes per sample), simple	·Data reliability questionable ·Lack of good carbon tetrachloride at SWCC gave high background	x
TOC method	·Small samples (several tens of microliters) ·Quick (10 minutes per sample), simple	·High background in sea water samples gives lower detection limit of several ppm ·Poor reproducibility in SWCC equipment (due to manual injection ?)	△
GC method	·Nothing special	·Low sensitivity (lower detection limit 5 ppm) ·Long measuring time (several tens of minutes per sample)	x
Fluorophotometry	·High sensitivity (lower detection limit 10 ppb) ·High reliability ·Good reproducibility ·Quick (10 minutes per sample)	·Complex operation ·Needs large samples (50 ml)	○ △～x (Beaker scale)

* × no good
△ applicable in some case
○ good

3. Summary

1) This research was characterized by the extremely low oil contents measured and the extremely large number of samples, which necessitated the establishment of a method of measurement which is sensitive and quick. As a result of studying several methods of measurement, TOC and fluorophotometry were selected for this research.

2) The TOC method is quick and comparatively sensitive and it requires small samples but the background from inorganic carbon in sea water is high.

3) Quick and sensitive with good reproducibility, fluorophotometry is the most suitable method for this study. However, comparatively large samples (50 ml) are required and it is not suitable for beaker scale experiments.

4. References:

(1.1) Japan Industrial Standards JIS K0102 59–64, 1993, Japan Industrial Standards Committee
(1.2) Japan Industrial Standards JIS K0102 65–66, 1993, Japan Industrial Standards Committee
(1.3) Shimadzu Corporation TOC–5000 User Manual

8.1.2.B. Oil Removal Experiment

(8.1.2.B)

Contents

List of Tables

List of Figures

1. Selection of Method

1.1 Comparison with Other Methods

(1) **Objective**

To study the effectiveness of the coagulation filtration method as a means of removing oil from oil-dispersed sea water.

(2) **Experimental Method**

Apparatus and Reagents

Ultrasonic homogenizer (Ultrasonic Engineering USH-300Z20S)
Peristaltic pump (Tokyo Rikakiki RP-1000)
Glass column (Shibata Kagaku HLC-20S; ϕ 2 cm, L = 30 cm)
TOC analysis gauge (Shimadzu TOC-500)
Silicon tube
Ferric chloride (Fisher, Anhydrous purified grade)
Sea water
Fuel oil A
Sand (0.6 mm)

Oil Content Measuring Method

TOC method

Procedure

The following procedures were carried out.

1) Preparation of oil-dispersed sea water

- While circulating 1 L of sea water inside an ultrasonic homogenizer with a peristaltic pump, 2.5 ml of fuel oil A was injected into the silicon tube containing the sea water and the sampled water was then subjected to 10 minutes of ultrasonic treatment.
- The concentration of oil in the rich oil-dispersed water thus obtained was adjusted to about 30 ppm by diluting with sea water.

2) Evaluation of oil-removing capability

When Coagulant Was Not Used

- Oil–dispersed sea water diluted to about 10 ppm was passed through a sand–filled glass mini column by means of the peristalic pump, and the concentration of oil was measured at the inlet and outlet of the column.

When Coagulant Was Used

- Ferric chloride was added to oil–dispersed sea water that had been diluted to about 30 ppm. The sample water was stirred for 1 minute at high speed (about 100 rpm) and then for 30 minutes at slow speed (about 40 rpm).
- While continuing the slow stirring, the above sample water was passed through a sand–filled, glass mini column by means of the peristalic pump, and the concentration of oil was measured at the inlet and outlet of the column.

Experimental Conditions

Column size : ϕ 2 cm, L = 30 cm
Filter medium : Sand (0.6 mm)
Height of filter medium : 20 cm
Flow rate : 3.1 L/hr. (LV 10 m/hr., SV 50 /hr.)

(3) Results and Discussions

There are various ways of treating oily waste water, but there are so many types of oily waste water that the method of treatment is more or less selected on the basis of such general factors as the required properties and quality of the processed waste water and the cost. With waste water in which oil is already floating or in which oil will in time float to the top, or in other words, with waste water in which the oil and water are easily separated, it is relatively simple to remove the oil content. In this case, in order to improve separation efficiency, the main objective in treatment is to find a way to enlarge the size of the oil droplets to make them float more quickly to the top. For instance, when the oil droplets are big, treatment is possible by simply letting the water stand or by natural separation of API, CPI, etc.. The limit of the size of the oil droplets that can be treated in this way, however is said to be somewhere from 100 μmm to 30 μmm. When the size of the oil droplets are larger than this, they are given a coarsening treatment using such equipment as a coalescer, etc.. When this is done, however, the lower limit of the oil droplet size that can be removed is said to be 10 μmm.

In the case of dispersed oil which consists of small droplets, or of emulsifying oil and soluble oil which have many surface active agents, the oil can be separated either by salting it out with the addition of large quantities of salt, by adding acid and making the oil emulsion break, or by adding inorganic or high-polymer coagulants.

Oily waste water in the emulsion state has conventionally been treated by the coagulation method. This process entails destroying the emulsified state by adding inorganic coagulants such as iron salt, aluminum salt or highly dispersive silicic acid, and, at the same time, removing the oil by coagulating it with metal hydroxides. The floc obtained by this means is separated by coagulation sedimentation, coagulation floatation, coagulation filtration, and other methods.

As a pretreatment system in an actual plant, the coagulation filtration method, that was mentioned in 1.2 "Pretreatment System in Actual Plant", is employed. Here the object of the pretreatment is not the removal of oil but removal of suspended matter that exists in sea water. Although there has been no report of the coagulation filtration method being used to remove oil dispersed in sea water, if the coagulation filtration method can be applied to this treatment, the pretreatment facilities of actual plants can be put to effective use.

Fig. 1 shows the difference in oil removal when a coagulant is used and when it is not. As can be seen, oil removal capability was much higher when a coagulant was used than when it was not. The reason for this is believed to be that when a coagulant was not used, oil removal was limited to the oil droplets in the test sample that adhered to the sand, whereas when a coagulant was used, the floc created by the addition of coagulant captured practically all of the oil droplets, and the floc was then removed by the sand.

By comparing the two, it is believed that although the capability of the oil droplets alone to adhere to the filter medium is not that good, the droplets are susceptible to being captured by floc.

From the results of this experiment, it is clear that the coagulation filtration method is an extremely effective way of removing oil from oil-dispersed sea water.

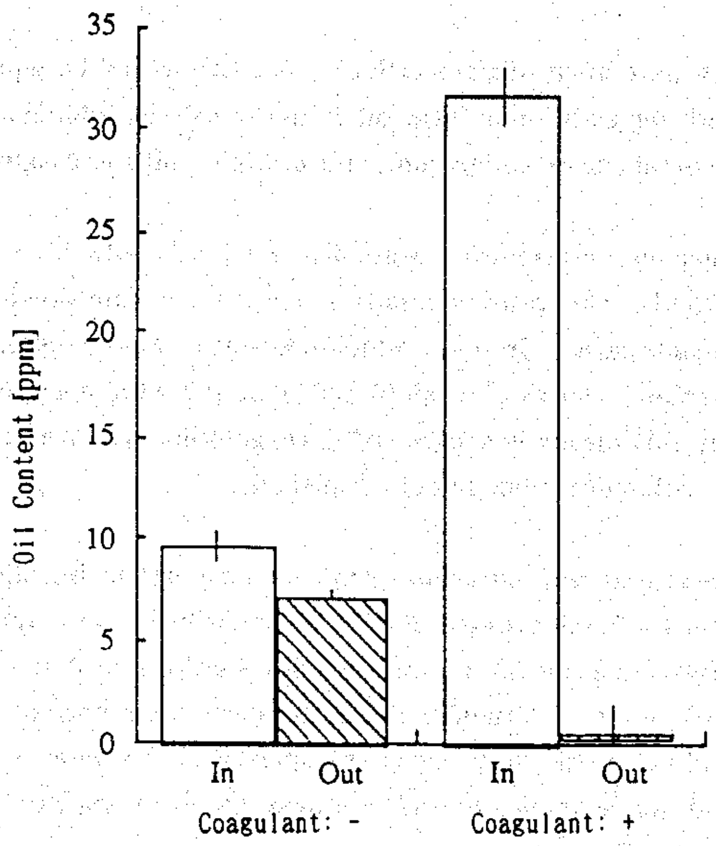


Fig. 1 Oil Removal by Sand Filtration (Mini Column)

1.2 Pretreatment System in Actual Plant

(1) Objective

From the results of documented studies, it is believed that the coagulation treatment employed in this research is a suitable method for treating oil. Although this method is already being employed in actual plants, it is not being used for removing oil. Instead it is being used for the removal of the suspended matter that exists in sea water. Here we will examine the pretreatment systems being employed with actual equipment.

(2) Results

SWCC operates 5 reverse osmosis sea water desalination plants on the Red Sea coast.

1.	Al Birk	2275 m^3	Commenced operating in March 1983
2.	Umm Luji	4400 m^3	Commenced operating in March 1986
3.	Jeddah-1	56800 m^3	Commenced operating in April 1989

4.	Duba	4400 m^3	Commenced operating in June 1989
5.	Haql	4400 m^3	Commenced operating in Oct. 1989

As shown in Table 1, the water intakes of all of the above 5 plants are located in at water depth of 4 - 12 m. After disinfecting with chlorine, the sea water is pretreated by coagulation filtration. As shown here, SWCC employs a coagulation filtration method that uses inorganic coagulants to pretreat the sea water.

Ferric chloride 1.2 - 1.3 ppm (as Fe^{3+}), ferrous sulfate 0.57 and 3 ppm (as Fe^{3+}), and Magnifloc 573C 2.3 ppm, are used as coagulants. Anthracite (0.85 - 2.5 mm) and sand (0.45 - 1.35 mm) are used as filter media in pressurized double layer filtration and gravity-type sand filtration. To remove tiny particles of about 5 - 20 μmm in size that the sand filtration equipment can not remove cartridge filters are also provided in the after-stage of the filtration equipment,

Therefore, if it can be confirmed that coagulation filtration is an effective method for removing oil from sea water, and that even when there is an actual oil spill at sea, existing facilities can be used to deal with it.

Table 1 **Pretreatment at SWCC Sea Water Desalination Plants on the Red Sea Coast**

Description	Jeddah-1	Umm Luji	Haql	Duba	Al-Birk
Coagulant					
Chemical	$FeCl_3 \cdot 6H_2O$	None	$Fe_2(SO_4)_3$	$Fe_2(SO_4)_3$	Magnifloc 573C
Dosing rate [mg/L]	1.2-1.3		0.57	3	2.3
Filter #1					
Type	Gravity	Gravity	Pressure/Vertical	Pressure/Vertical	Pressure/Vertical
Material	Concrete	Concrete	Rubber lined steel	Rubber lined steel	Rubber lined steel
Anthracite Particle Size [mm]	0.9	0.85-0.95	1.14-2.5	1.40-2.5	
Anthracite Depth [cm]	60	20.32	50	60	
Sand Particle Size [mm]	0.45	0.55-0.65	0.71-1.25	0.71-1.25	1.35
Sand Depth [cm]	60	20.32	50	50	72
Filter #2					
Type	None	Pressure/Vertical	Pressure/Vertical	Pressure/Vertical	Pressure/Vertical
Material		Rubber lined steel	Rubber lined steel	Rubber lined steel	Rubber lined steel
Anthracite Particle Size [mm]		0.8-0.9	Nil	Nil	0.82
Anthracite Depth [cm]		25.4			40
Sand Particle Size [mm]		0.45-0.55	0.4-0.8	0.4-0.8	0.6
Sand Depth [cm]		25.4	90	90	40
Cartridge Filter					
Size [μm]	10	20	5	5	5
Change rate	Once/2-3 month	Once/3 month	Once/6 month	Once/6 month	Once/6 month
Housing Material	RTR	317 L	316 L	316 L	FRP

2. Study of Oil Removal by Coagulation Filtration

2.1 Comparison of Coagulants (Comparison of Ferric Chloride and Ferrous Sulfate)

(1) Objective

To select the coagulant to be used in coagulation filtration.

In 1991, a joint SWCC–JICA research project was conducted to study coagulants. The results of the research indicated that ferric chloride and ferrous sulfate were effective. Therefore, a comparative study was conducted on these two coagulants.

(2) Experimental Method

Apparatus and Reagents

Ultrasonic cleaner (Blackstone T–1.9, 5A, 0.6kVA)
TOC analysis gauge (Shimadzu TOC–500)
Jar tester (Philips & Bird)
Glass funnel
Beaker
Pipette
Conical flask (1 L)
Glass wool (Pyrex fiber glass, sliver 8 micron)
Fuel oil A
Sea water
Ferric chloride (Fisher, Anhydrous purified grade)
Ferrous sulfate (BDH, Technical grade)

Oil–Content Measuring Method

TOC method

Procedure

1) Preparation of oil–dispersed sea water

Oil–dispersed sea water was prepared by the procedure shown in Fig. 2.

Sea water 1 L (using 1 L Erlenmeyer flask)
↓ ← Fuel oil A 5 ml
Ultrasonic treatment (ultrasonic washer) 20 minutes
↓
Leave standing for 10 minutes
↓
Collect 650 ml from bottom of receptacle
↓
Leave standing for 60 minutes
↓
Measure TOC
↓
Dilute with sea water

Fig. 2 Method of Preparing Oil–Dispersed Sea water

2) Coagulation Filtration Test

Coagulation filtration tests were performed by the procedure shown in Fig. 3.

Oil–dispersed sea water 600 ml/1 L beaker
↓ ← Ferric chloride or ferrous sulfate
↓ 0.5, 1, 1.5 ppm (as Fe^{3+})
Rapid stirring (100 rpm for 1 minute)
↓
Slow stirring (40 rpm for 20 minutes)
↓
Filtered 125 ml through glass wool (0.18 g)
↓
TOC measurements

Fig. 3 Coagulation Filtration Test Procedure

(3) Results and Discussions

Fig. 4 shows the relationship of the Fe^{3+} concentration in the respective coagulants and

oil removal rate. As the coagulating reaction consisted of hydration of the Fe3+ in the coagulant in the water and its transformation into floc induced by ferric hydroxide hydrates, the comparison was done here on Fe3+ concentration.

By adding about 1 – 1.7 ppm as Fe^{3+}, both ferric chloride and ferrous sulfateremoved about 80% or more of the oil, and there was relatively little difference between them. Presently, both are being used in actual plants. Since ferric chloride is a material that is already furnished and available at the site, however, we decided to use ferric chloride in this study.

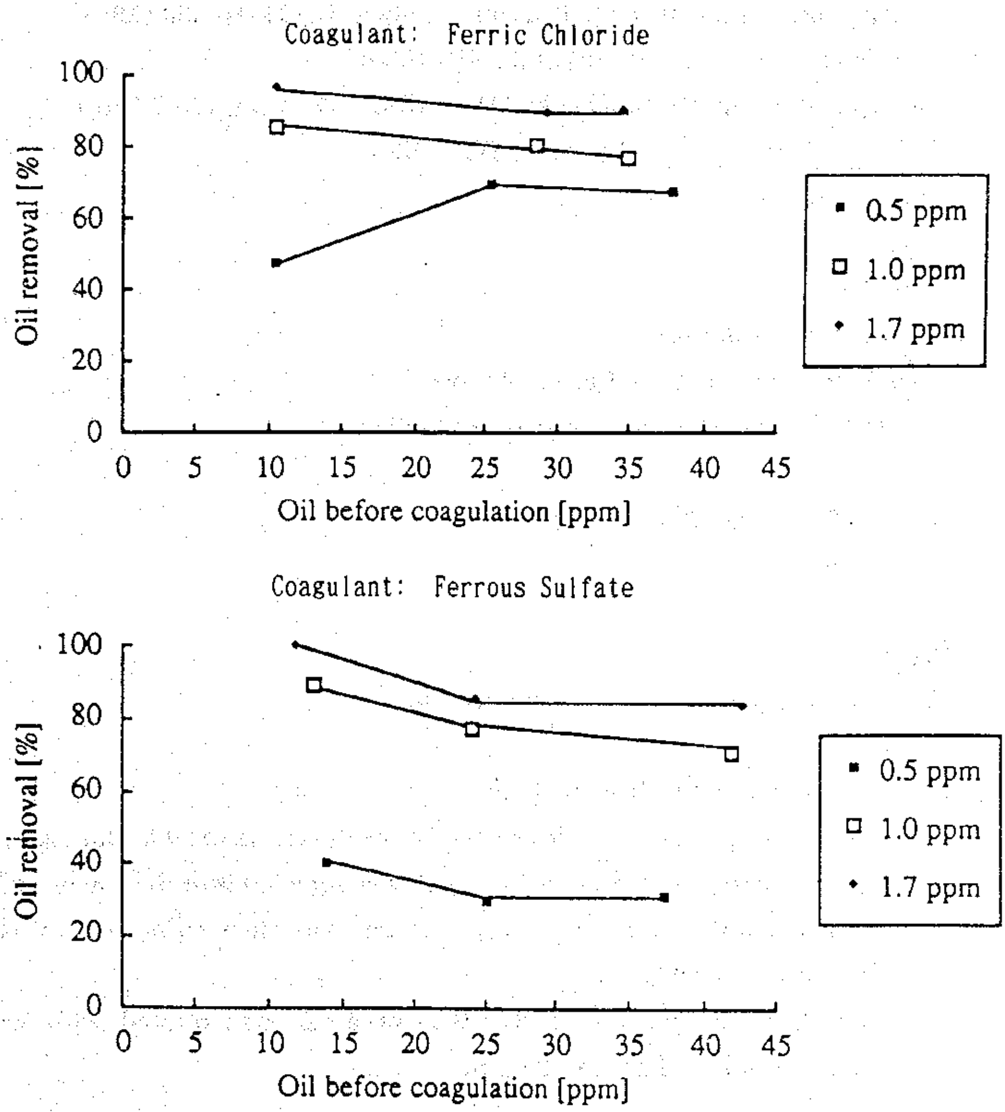


Fig. 4 Relationship of Amount of Coagulant Added (Converted to Fe^{3+}) to Oil Removal Rate

2.2 Study Using Mini Column

(1) Objective

To study with a small-scale experimental system whether or not oil was effectively removed when the coagulation filtration method was applied to remove oil from oil-dispersed sea water.

(2) Experimental Method

Apparatus and Reagents

Ultrasonic homogenizer (Ultrasonic Engineering USH-300Z20S)
Peristalic pump (Tokyo Rikakiki RP-1000)
Glass column (Shibata Kagaku HLC-20S: ϕ 2 cm, L = 30 cm)
TOC analysis gauge (Shimadzu TOC-500)
Silicon tube
Sea water
Fuel oil A
Anthracite (1.0 mm)
High polymer filter medium (1.0 mm)
Ferric chloride (Fisher, Anhydrous purified grade)

Oil-Content Measuring Method

TOC method

Procedure

The following procedures were carried out.

1) Preparation of oil-dispersed sea water

- While circulating 1 L of sea water inside an ultrasonic homogenizer with the peristalic pump, 2.5 ml of fuel oil A was injected into the silicon tube containing the sea water, and the sample water was then subjected to 10 minutes of ultrasonic treatment.
- The rich oil-dispersed water thus obtained was diluted with sea water to a concentration of about 30 ppm.

2) Evaluation of oil-removal capability

- 3 ppm of ferric chloride (as $FeCl3$) was added to oil-dispersed sea water which had been diluted to about 30 ppm by the above method. The sample water was subjected to 1 minute of rapid stirring (about 100 rpm) and then to 30 minutes of slow stirring (about 40 rpm).

- While continuing the slow stirring, the above oil-dispersed sea water was passed through a glass mini column filled with each of the adsorbents by means of the peristalic pump, and the oil concentration was measured at the inlet and outlet of the column.

<u>Experimental Conditions</u>

Column size	:	ϕ 2 cm, L = 30 cm
Filter medium	:	Sand (0.6 mm)
Filter medium height	:	20 cm
Flow rate	:	3.1 L/hr. (LV 10 m/hr., SV 50/hr.)

(3) Experimental Results

As shown in Fig. 5, no matter which filter medium was used, the oil content of approximately 30 ppm dropped to about 1 – 2 ppm, proving that the method was extremely effective. However, because the scale of this test was small and accurate oil content measurements by fluorophotometry could not be made, the difference in the oil-removal capabilities of the respective filter media was not clear. We believe that more detailed data can be obtained by carrying out large-scale tests and making measurements by means of fluorophotometry.

At any rate, from these results we believe that bench-scale oil removal tests using pretreatment facilities to carry out coagulation filtration can also be expected to be fully effective.

(8.1.2.B)

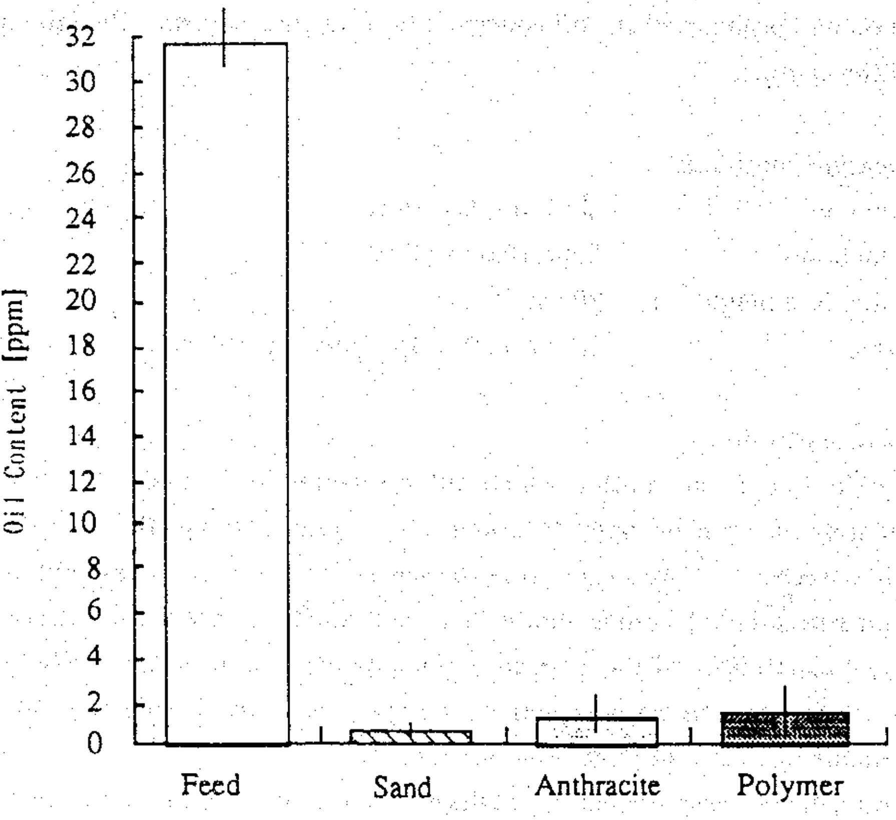


Fig. 5 Coagulation Filtration Using Mini Column

3. Study for the Optimization of Coagulation Conditions

3.1 Experiment with a Beaker Scale

(1) Background and Objectives

To remove oil efficiently with the coagulating filtration method, it is considered necessary to sufficiently coagulate the oil (oil drops) in oil–dispersed sea water as flocs. To remove dispersed oil more efficiently, this experiment examined the optimization of coagulation conditions such as the concentration of coagulant and the reaction time was examined using a beaker scale, for the purpose of removing dispersed oil efficiently.

(2) Experimental Method

Apparatus and Reagents

Ultrasonic cleaner
Fluorophotometer (Nippon Bunko FP–770)
Microscope (Olympus BHS–PC–B–SW)
Jar tester
Separating funnel (100 ml)
Glass funnel
Separating funnel shaker (Iwaki KM–SHAKER, V–SN)
Filter paper (Advantec 5A, 11 cm)
Measuring flask (25 ml)
Sea water
Fuel oil A
Ferric chloride (Sankei Kasei)
Isooctane (Kanto Chemical, for fluorometric analysis)
Sulfuric anhydride natorium (Wako, superior quality)

Oil Content Measuring Method

Fluorophotometry

Procedures

1) Preparation of oil–dispersed sea water

Oil–dispersed sea water of about 10ppm was prepared with the procedures indicated in Fig. 6.

600 mL sea water (A 1 L conical flask was used.)
↓ ← 3 mL fuel oil A
Ultrasonic treatment (ultrasonic washer) for 15 minutes
↓
Leave standing for 10 minutes
↓
Took 400 ml from the bottom of the container
↓
Diluted with sea water to about 10 ppm

Fig. 6 Preparation of Oil–Dispersed Sea Water

2) Examination of the conditions of coagulation treatment

- Ferric chloride (as $FeCl_3$) was added to about 300 ml oil–dispersed sea water of about 10 ppm at the concentration of 5 – 50 ppm.
- After quick agitation (100 rpm, 1 minute), the solution was slowly agitated (40 rpm) and the floc size and the transparency of the test water were checked.

Measuring Conditions

Slit width : Excitation 10 nm, Fluorescence 10 nm
Excitation wavelength : 310 nm
Fluorescence wavelength : 343 nm

(3) Results and Discussions

Figures 7 and 8 indicate the relation of the coagulation reaction time and the floc size, and the relation of the coagulation reaction time and the transparency of the test water at various concentrations of coagulant.

When the reaction time was about 10 minutes, the concent–ration of coagulant had to be at least 20ppm for the coagulation reaction to progress sufficiently.

There is a high correlation between the floc size and the transparency of the test water; when the floc size becomes about D5 (1.5–2.25 mm), the test water becomes very transparent. With the floc size at of this level, almost all oil drops are contained in the flocs. Even at this level, however, some oil drops do remain isolated in the water. It is not possible to completely remove these isolated oil drops.

This is because no collision of flocs and isolated oil drops has been observed. It is estimated that when the concentration of coagulant is increased further, when the

reaction time is further extended, or when the agitation efficiency is raised, the problem of isolated oil drops will be solved. If these measures are taken, however, the cost will increase because the frequency of backwash will have to be raised due to the increase of flocs, and the amount of water required for backwash will increase. Consequently, the balance between the inconveniences caused by taking measures to completely remove isolated oil drops and the beneficial effects achieved by the improvement in the quality of the pretreated water will have to be considered when determining the target level for the coagulation reaction.

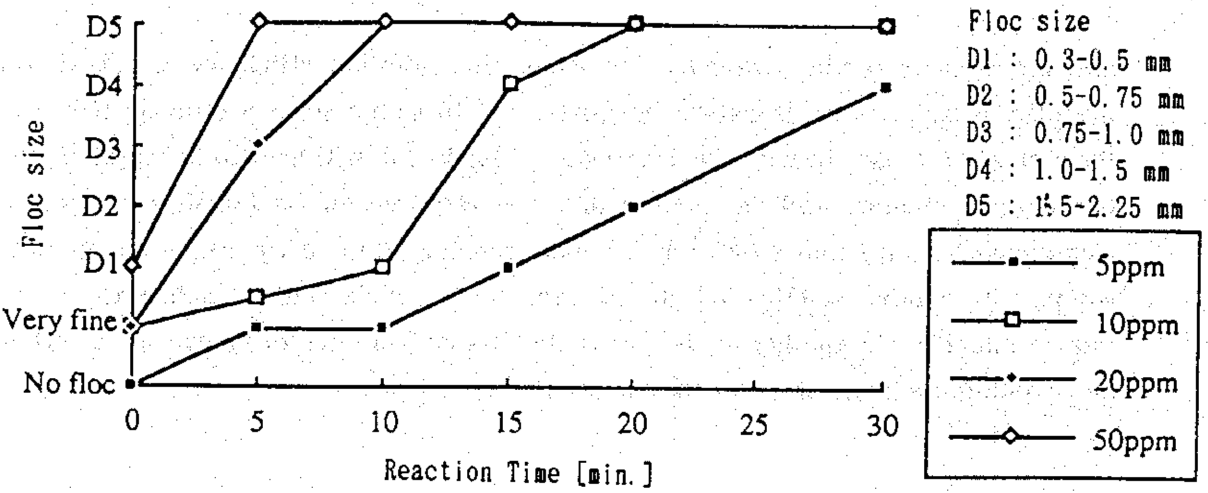


Fig. 7 Relation of the Coagulation Reaction Time and the Floc Size (Coagulant : FeCl3)

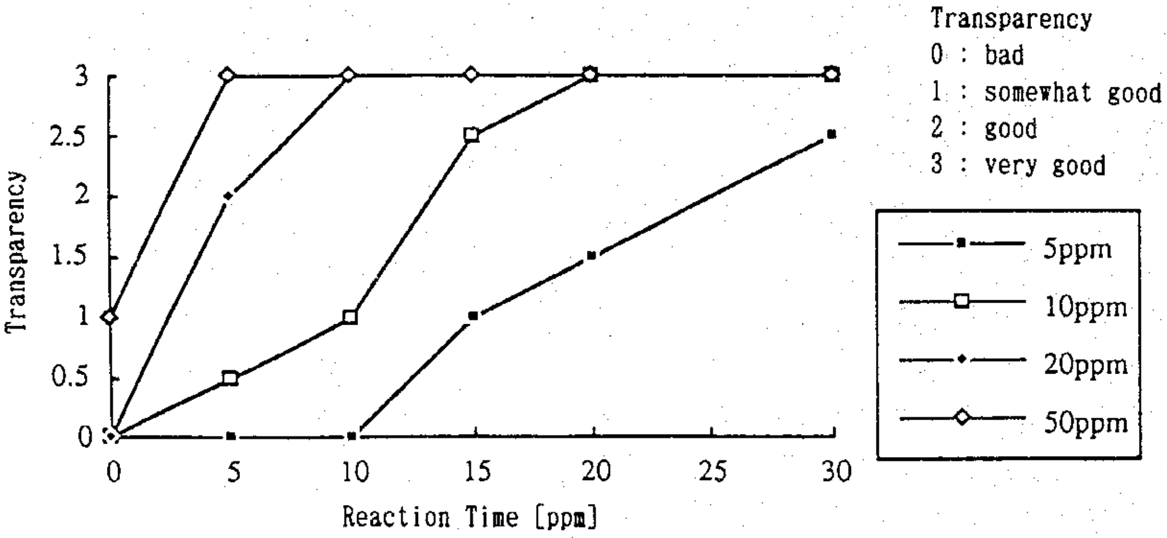


Fig. 8 Relation of the Coagulation Reaction Time and Transparency (Coagulant : FeCl3)

3.2 Experiment with a Bench Scale

3.2.1 Examination of the Flocculation Method

(1) Objectives

When coagulating filtration was conducted using pretreat-ment equipment, it became clear that flocs generated by coagulation treatment are very fragile and are pulverized by the shearing force that they are subjected to as they travel through the liquid feed pump. It is estimated that coagulating filtration will not be conducted effectively when flocs are pulverized. Examination of a flocculation method applicable to this equipment was, therefore, carried out.

(2) Experimental Method

Apparatus and Reagents

Oil–adding and –adjusting device
Oil–adsorbing and –removing device
Fluorophotometer (Nippon Bunko FP–770)
Microscope (Olympus BHS–PC–B–SW)
Separating funnel (100 ml)
Glass funnel
Separating funnel shaker (Iwaki KM–SHAKER, V–SN)
Filter paper (Advantec 5A, S11 cm)
Measuring flask (25 ml)
Sea water
Fuel oil A
Isooctane (Kanto Chemical, for fluorometric analysis)
Sulfuric anhydride natorium (Wako, superior quality)
Sand (0.6 mm)
Ferric chloride (Sankei Kasei)

Oil Content Measuring Method

Fluorophotometry

Procedures

Procedures taken are as follows:

1) **Preparation of oil–dispersed sea water**

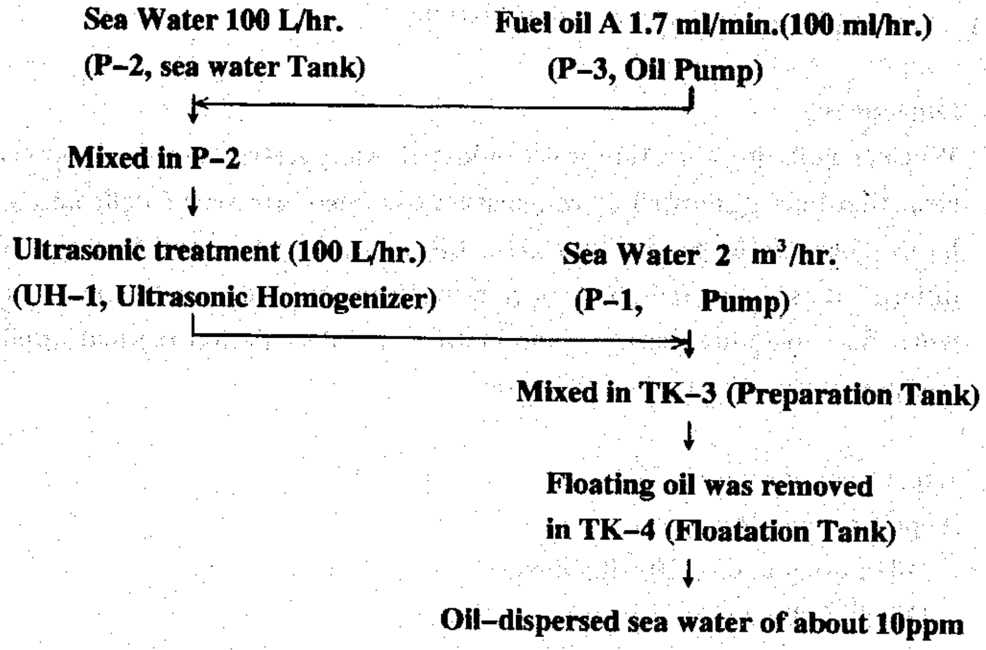


Fig. 9 Preparation of Oil–Dispersed Sea Water with an Oil Adding and Adjusting Device

2) **Examination of the coagulant–adding method**

After adding coagulant (ferric chloride) to the oil–dispersed sea water prepared with the above–mentioned procedures, the sea water was fed through a sand filtration column. Then, the change in the concentration of the oil brought about with time was measured at the inlet and the outlet of the column.

The following two types of coagulant–adding methods were examined. (Fig. 10)

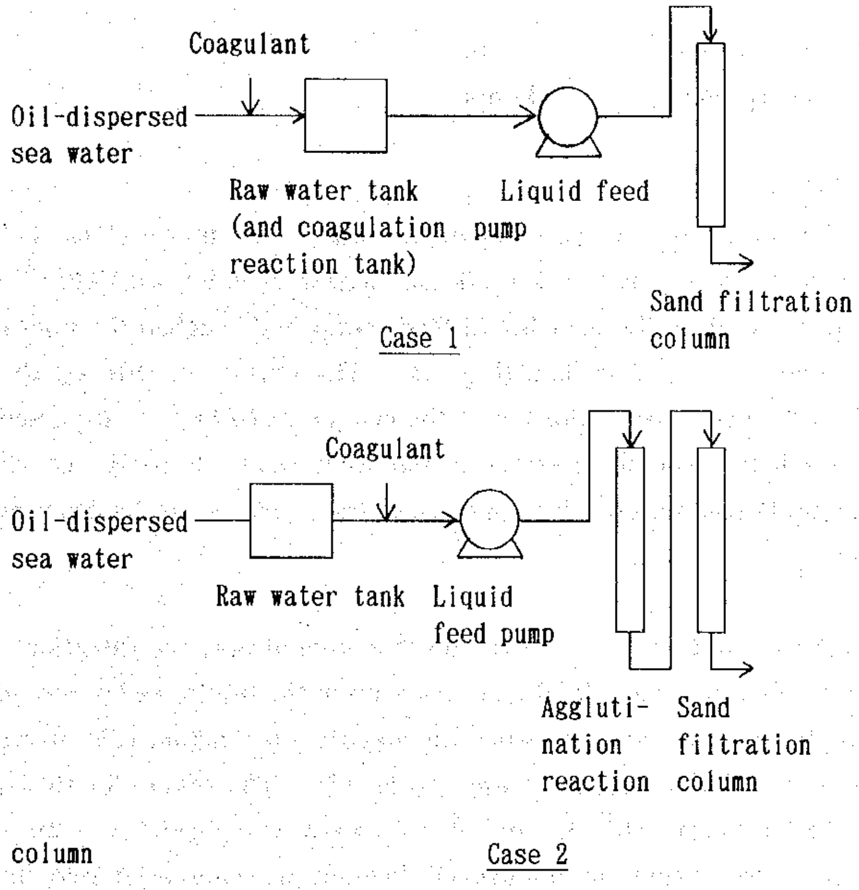


Fig. 10 Examined Flows of Coagulant–Adding Method

Experimental Conditions

Column size : S10 cm, L 100 cm
Filter media : Sand
Height of filter media : 50 cm
Water travel speed : 80 L/hr. (LV 10m/hr., SV 20/hr.)
Coagulant : Ferric chloride
Concentration of coagulant added : 10 ppm (as FeCl3)

(Conditions for Case 2 only)

Coagulation reaction column : S10 cm, L 100 cm; one column
Coagulation reaction time : 9 minutes (time required for water to reach the inlet of the sand filtration column)

Measuring Conditions

Slit width : Excitation 10 nm, Fluorescence 10 nm

Excitation wavelength : 310 nm
Fluorescence wavelength : 343 nm

(3) Results and Discussions

When coagulant was added upstream of the liquid feed pump (Case 1), flocs grew sufficiently in the raw water tank (and coagulation reaction tank)(Fig. 11), but the flocs were pulverized by the next liquid feed pump and reached the inlet of the sand filtration column as very fine flocs (Fig. 12). The reason for this is estimated to be that the flocs formed by the addition of the coagulant to the oil–dispersed sea water were very weak in mechanical strength and were easily destroyed by the shearing force in the liquid feed pump. The pulverized flocs then reach the filter media before they regrow.

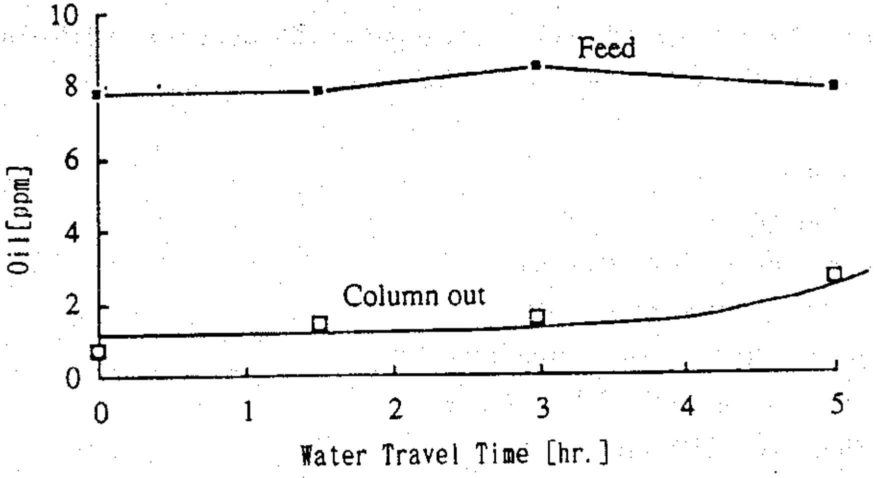
Increase in the size of flocs was confirmed at the inlet of the sand filtration column when coagulant was added just upstream of the liquid feed pump and pump–mixing was then carried out, and when an coagulation reaction column was installed brfore the sand filtration column (Case 2),(Fig. 13). The reason for this is estimated to be that the flocs grew while the oil–dispersed sea water which was mixed with the coagulant in the liquid feed pump travelled through the coagulation reaction column.

In the flow of "Case 1" of Fig. 3.10, the concentration of oil in the water at the outlet of the sand filtration column began rising about 3 hours after water started travelling. In the flow of "Case 2" of Fig. 3.10, however, the concentration of the oil at the outlet hardly changed for about 5 hours (Fig. 14). This indicates that when flocs are too small, the penetration of flocs (+ oil drops) through the filter media starts too early, and effective coagulating filtration cannot be achieved.

It is estimated that in the flow of "Case 2", the flocs larger to some extent and that most of the flocs (+ oil drops) were kept in the void of the filter media. The penetration of the flocs, therefore, did not start as early as in the case of small flocs.

Based on the results of Figures 12 – 14, it is considered best to add coagulant just upstream the liquid feed pump (parentheses as in Case 2), to then have flocs formed by letting water travel through the coagulation reaction tower after pump–mixing, and then to carry out filtration. Under the present conditions, however, flocs at the inlet of the filtration column do not become as large as the flocs in the raw water tank

Sand Filtration in "Fig. 10 Case 1"



Sand Filtration in "Fig. 3.10 Case 2"

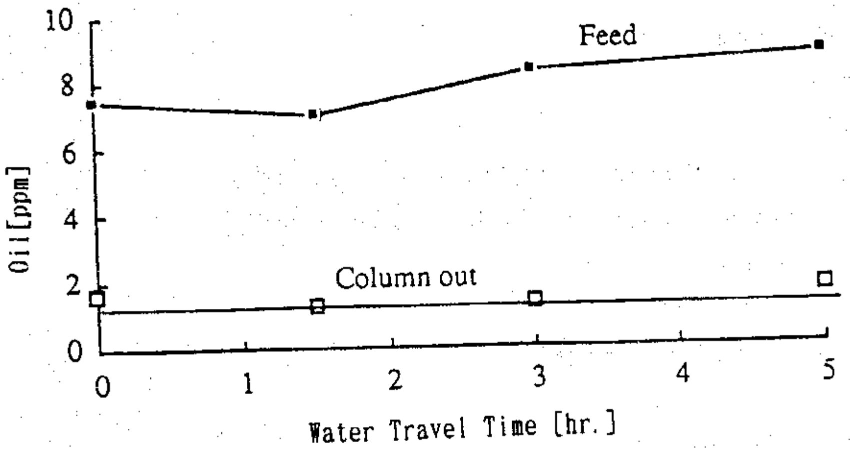


Fig. 14 Sand Filtration by Two Types of Coagulant Addition

3.2.2 Examination of Agglomeration Conditions

(1) **Objectives**

Based on the coagulation optimizing conditions ascertained from the results of "3.1. Examination with a Beaker Scale"; coagulating filtration was carried out using a 10cm column to check the oil-removing capacity.

(2) **Experimental Method**

Apparatus and Reagents

Oil-adding and -adjusting device
Oil-adsorbing and -removing device
Fluorophotometer (Nippon Bunko FP-770)
Microscope (Olympus BHS-PC-B-SW)
Separating funnel (100 ml)
Glass funnel
Separating funnel shaker (Iwaki KM-SHAKER, V-SN)
Filter paper (Advantec 5A, S11 cm)
Measuring flask (25 ml)
Sea water
Fuel oil A
Isooctane (Kanto Chemical, for fluorescence analysis)
Sulfuric anhydride natorium (Wako, superior quality)
Sand (0.6 mm)
Anthracite (1.0 mm)
Ferric chloride (Sankei Kasei)

Oil Content Measuring Method

Fluorophotometry

Procedures

Procedures taken are as follows:

1) Preparation of oil-dispersed sea water

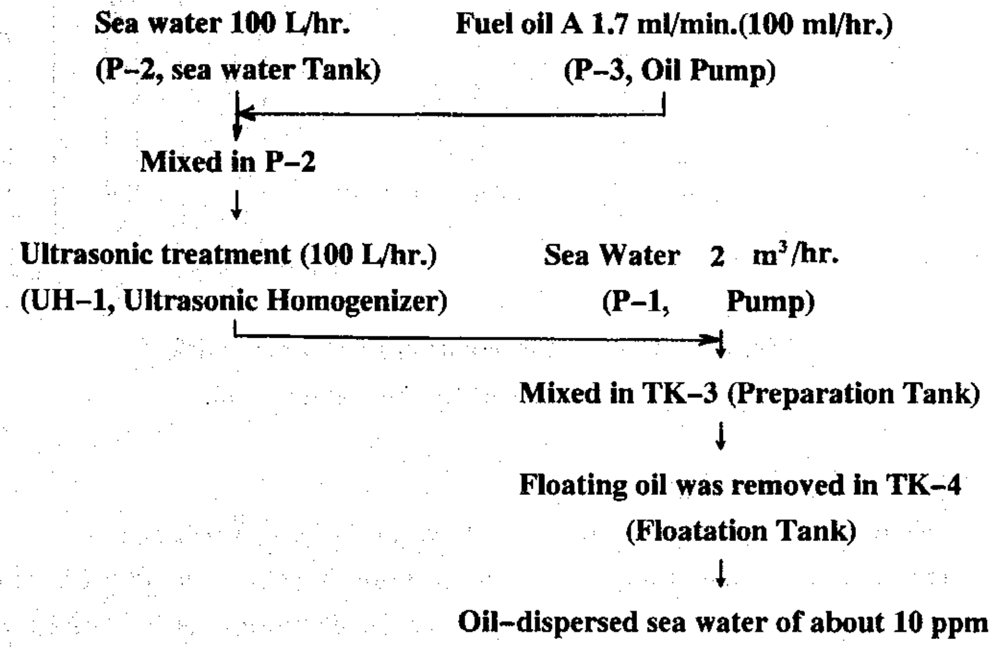


Fig. 15 Preparation of Oil-Dispersed Sea Water with Oil-Adding and -Adjusting Device

Coagulant was added to the prepared oil-dispersed sea water, and the following items were examined.

<u>Common Experimental Conditions</u>

Column size : S10 cm, L 100 cm
Water travel speed : 80 L/hr.(LV 10 m/hr., SV 20/hr.) and
40 L/hr.(LV 5 m/hr., SV 10 hr.)
Coagulant : Ferric chloride
Concentration of the coagulant added : 10, 20 ppm (as FeCl3)

2) Coagulation Effect Achieved by the Addition of Coagulant

- **Soon after adding 10 or 20 ppm coagulant (ferric chloride) to oil-dispersed sea water prepared using the above-mentioned procedures, the water was mixed by a liquid feed pump and fed through three empty 10 cm-colmns (Fig. 16). The reaction time in each column was adjusted by changing the flow velocity.**

- The size of the flocs was checked in each column.

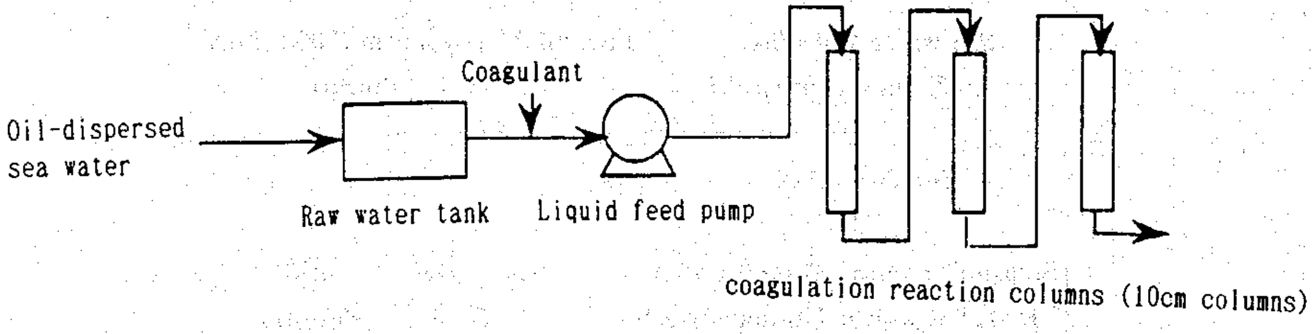


Fig. 16 Flow of Flocculation Experiment with Coagulation Reaction Column Unit

<u>Experimental Conditions</u>

coagulation reaction column : S10 cm, L 100 cm; 3 columns
coagulation reaction time : 5, 10, 15 minutes (LV 10 m/hr.,SV 20/hr.)
and 10, 20, 30 minutes (LV 5 m/hr.,SV 10/hr.)

3) Oil–removing capacity depending on coagulation conditions

- Soon after adding 10 or 20 ppm coagulant (ferric chloride) to oil–dispersed sea water prepared using the above–mentioned procedures, the water was mixed by a liquid feed pump and fed travel through a 10cm column unit (Fig. 17). The first column was used as an coagulation reaction column. The second and the third columns were used as coagulating filtration columns. The reaction time in each column was adjusted by changing the flow velocity.
- Samples were taken at the outlets of each of the columns respectively and the oil content of each sample was measured.

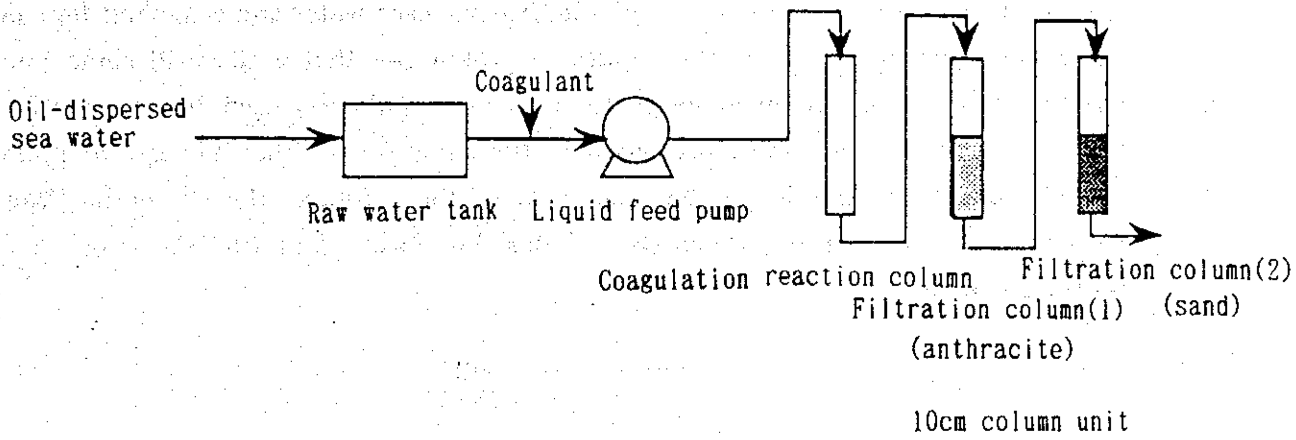


Fig. 17 Flow of Oil–Removing Experiment by Coagulating Filtration Method

Experimental Conditions

Filter media : anthracite (1.0 mm), sand (0.6 nmm)
Height of filter media : 50 cm
coagulation reaction time : 9 minutes (LV 10 m/hr.,SV 20/hr.) and 15 minutes (LV 5 m/hr.,SV 10/hr.)

Measuring Conditions

Slit width : Excitation 10 nm, Fluorescence 10 nm
Excitation wavelength : 310 nm
Fluorescence wavelength : 343 nm

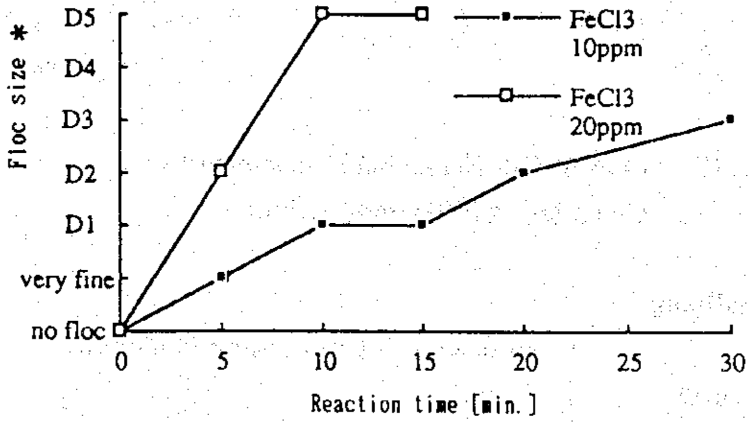
(3) Results and Discussions

1) Coagulation Effect Achieved by the Addition of Coagulant

Fig. 18 shows the relation of the reaction time and the maximum floc size observed for each concentration of coagulant. As long as the reaction time was the same, maximum floc observed was larger when coagulant of 20 ppm was used, than the when coagulant of 10 ppm was used. This indicates that the coagulation effect is larger when the concentration of coagulant is higher.

As the flocs observed in this experiment were extremely fine, however, the influence of the concentration of coagulant or of the reaction time was not confirmed. It is estimated that the flocs became so fine for the following reasons. When a column is

used as an coagulation reaction column, oil-dispersed sea water and coagulant flow in the column just like laminar flow, and the probability that a floc will come into contact with another is much lower than when a beaker is used for coagulation reaction. Flocs do not, therefore, grow in the column. As the diameter of pipes which connect columns is smaller than that of the columns, the streamline flow velocity rises and causes an increase of shearing force, And this shearing force pulverizes the flocs.



***: The floc size indicated above is that of the maximum floc observed in the sample. <u>(Irrespective of the concentration of coagulant or the reaction time, most flocs were very fine.)</u>**

Fig. 18 Relation of the Concentration of Coagulant and the Reaction Time with the Floc Size (Coagulation Reaction Column was Used.)

2) Oil-removing capacity depending on coagulation conditions

Fig. 19 shows oil-removing capacity under varied operation conditions (coagulation conditions). Under any condition, oil-removing capacity hardly fluctuated. By coagulating filtration, about 1 to 2 ppm oil content was removed, but no more could be removed. When a large amount of coagulant is used, the cost increases and the necessity for more frequent backwashes in arises because the amount of flocs generated increases and the penetration time is shortened by the coagulant. It is, therefore, considered better to add 10 ppm coagulant than to add 20 ppm.

When samples were observed by a microscope, a large number of flocs with large quantities of oil attached to them observed in the sample taken at the inlet were removed, and no oil drops were observed in the samples taken at the outlet of the first filtration (anthracite) and the second filtration columns (sand) (Fig. 20 – 22).

(8.1.2.B)

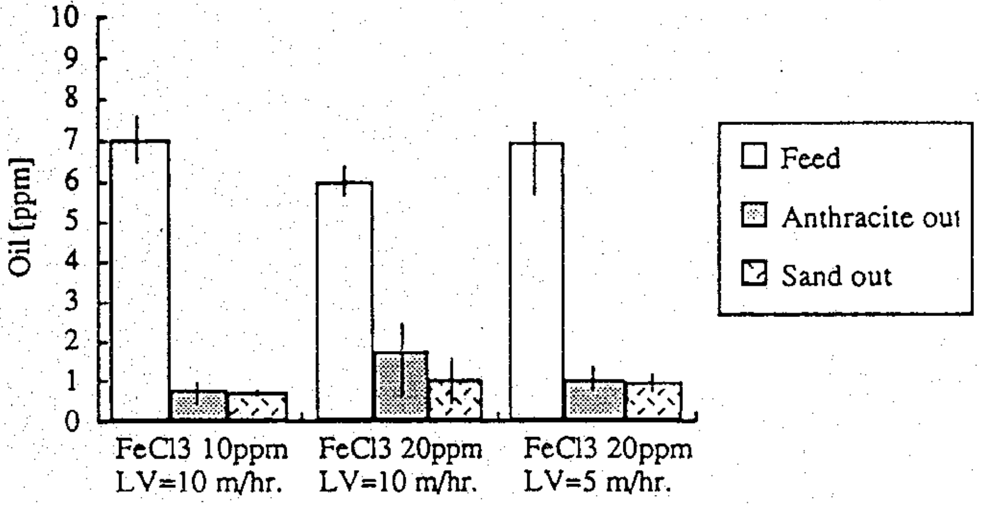


Fig. 19 Comparison of Oil–Removing Capacity under Different Coagulation Conditions

Fig. 20 Inlet of the Filtration Column (1) (x100)

(8.1.2.B)

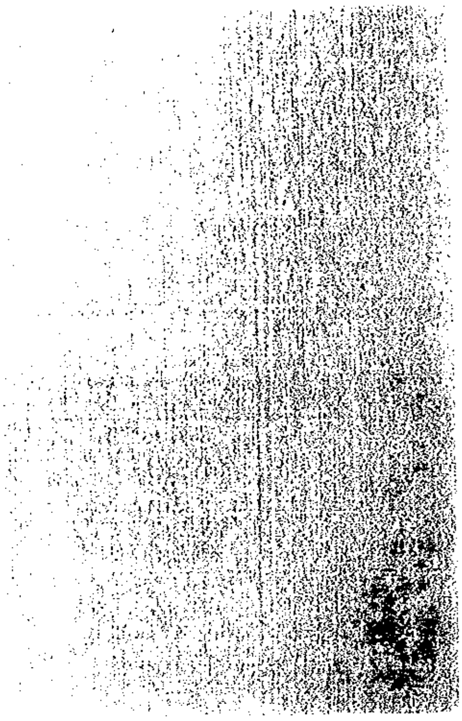


Fig. 21 Outlet of the Filtration Column (1) (x100)

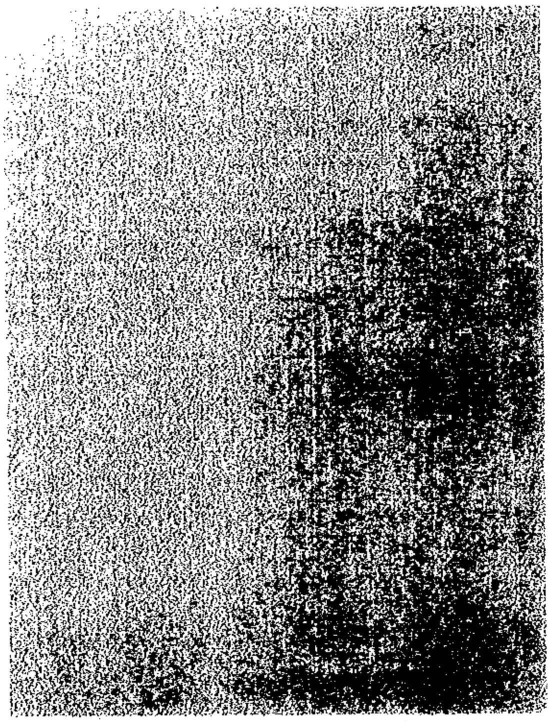


Fig. 22 Outlet of the Filtration Column (2) (x100)

From the above results, the following are estimated.

- When fuel oil A is dispersed, the components of the oil are separated as dispersed oil and soluble oil. These two types of oil exist in sea water at a certain ratio. Dispersed oil is observed as oil drops by a microscope, but soluble oil cannot be observed.
- By coagulation reaction, most dispersed oil is caught in the flocs of ferric hydroxide generated by coagulant (ferric chloride).
- Oil drops (dispersed oil) caught by flocs are removed in the anthracite column, but soluble oil is not removed. Soluble oil is not removed even in the next sand filtration column.
- It is impossible to remove soluble oil by the coagulating filtration method. Removal of soluble oil is beyond the capacity of the method.

To verify the above series of hypotheses, the following confirmation measures are required.

- Separate soluble oil from various oil in oil–dispersed sea water, measure the ratio of soluble oil, and confirm that the ratio of soluble oil is constant.
- Measure the amount of soluble oil in the sample of every step in the coagulating filtration treatment, and confirm that most oil contained in the sample after coagulation filtration treatment is soluble oil.

4. Assessment of soluble oil

(1) Objectives

We assumed, as a result of examining the flocculant filtration process for removing oil from oil-dispersed sea water, that there was unremovable oil even under optimum direct filtration conditions. We further assumed that most unremovable oil is soluble oil.

In order to confirm the above asssumption, we examined the properties of soluble oil after dispersed oil was removed by a membrane filtration process.

(2) Experimental Method

Apparatus and reagents

GC-MS analyzer
Fluorophotometer (Shimadzu RF-1501)
Microscope (Olympus VANOX-S, AH2)
Ultrasonic homogenizer (Ultrasonic Engineering USH-300Z20S)
Shaker (Yamato Scientific SA-31)
Separating funnel (100ml)
Glass funnel
Filter-paper (Advantec 5A, ϕ 11 cm)
Volumetric flask (25ml)
Beaker
Pipet
Membrane filter (Milipoa, ϕ 47 mm, Material: polycarbonate, pore sizes 0.4, 0.2 ϕ mm)
Filter holder (Milipoa, for ϕ 47mm filter, Material: polypropylene)
Syringe (50ml, Material: polypropylene)
Kuderna-Danish Concentrator
Sea water
Diesel oil No.2
Anhydrous sodium sulfate (Kanto Chemical, special grade)
Isooctane (Fisher Science, HPLC grade)
Carbon tetrachloride (BDH, analysis grade)
Methyl chloride (Fisher, Optima grade)

(8.1.2.B)

Oil content measuring method

Fluorophotometry

GC-MS analytical conditions

Analyzer : HP 5880-GC-MSD HP 5970B
Recoder : HP plotter 7475A
Column : HP 1 , 25m capillary
Quantity of injected volume : 3 ml
Temperature of column oven : 50℃
Temperature of interface : 280℃
Injection temperature : 250℃
Gradient of column temperature : 1) Initial : 50℃, 3 min.
2) Gradient : 10℃/min.
3) Finishing : 280℃, 10 min.

Measuring Conditions

Slit width : Excitation 10nm, fluorescence 10nm
Excitation wavelength : 305nm
Fluorescence wavelength : 336nm

Procedure

1) Preparation of oil-dispersed sea water

- While circulating one liter of sea water in an ultrasonic homogenizer with a peristaltic pump, inject 2.5ml of diesel oil into the silicone tube through which the sea water is circulating and continue the ultrasonic treatment for 10 minutes.
- Dilute the resulting concentrated oil dispersion with sea water to the concentration to be tested.

2) Selection of membrane filter

- Prepare 10 ppm oil-dispersed sea water according to 1).
- While shaking 50ml of above oil-dispersed sea water, extract with syringe from the bottom of the container.
- Connect syringe to the filter housing which is equipped with membrane filter, and apply pressure filtration.

  Observe precautions not to use excessive pressure which might result in forcing oil drops into the filtrate.

- Measure and compare oil content before and after the filtration by fluorophotometry.

3) Analysis of soluble oil characteristics

The diameter of oil drops in dispersed sea water, prepared with the ultrasonic wave method were approximately 1 to 3 μm. This dispersion was filtered through a 0.2 μm pore diameter membrane filter. We consider the filtrate to contain soluble oil.

- Using the procedure outlined in 1), prepare 10ppm oil-dispersed sea water.
- The oil-dispersed sea water from above is filtered through the 0.2 μm pore diameter membrane filter chosen in 2) while using suction filtration equipment.
- Analyze the component distribution by GC-MS

4) Determining the abundance ratio of soluble oil in oil-dispersed sea water.

- Prepare 10 ppm oil-dispersed sea water according to 1).
- Shake 50ml of above oil-dispersed sea water, extract with syringe from the bottom of the container.
- Connect syringe to the filter housing which is equipped with membrane filter, and apply pressure filtration.

  Observe precautions not to use excessive pressure which might result in forcing oil drops into the filtrate.
- Measure and compare oil content before and after the filtration by fluorophotometry.

(3) Results and Discussion

1) Selection of membrane filter

In Table 2, oil contents before and after filtration using membrane filters with two pore diameters is shown. From this and the domestic experiments' results, we found that there was not much difference in exiting oil, both the 0.2 μm and 0.4 μm pore diameter filters can filter out soluble oil. However, when excessive pressure is used in the filtration process, there is a possibility for oil drops to form and go through the membrane. Therefore, we decided to use pore diameter 0.2 μm as the possibility of this occurring was determined to be lower if a smaller pore diameter filter was used.

Table 2 Filtration of oil-dispersed sea water by membrane filters

Filter pore diameter [μm]	Oil content before filtration [ppm]	Oil content after filtration [ppm]
0.4	13	0.6
0.2	13	0.8

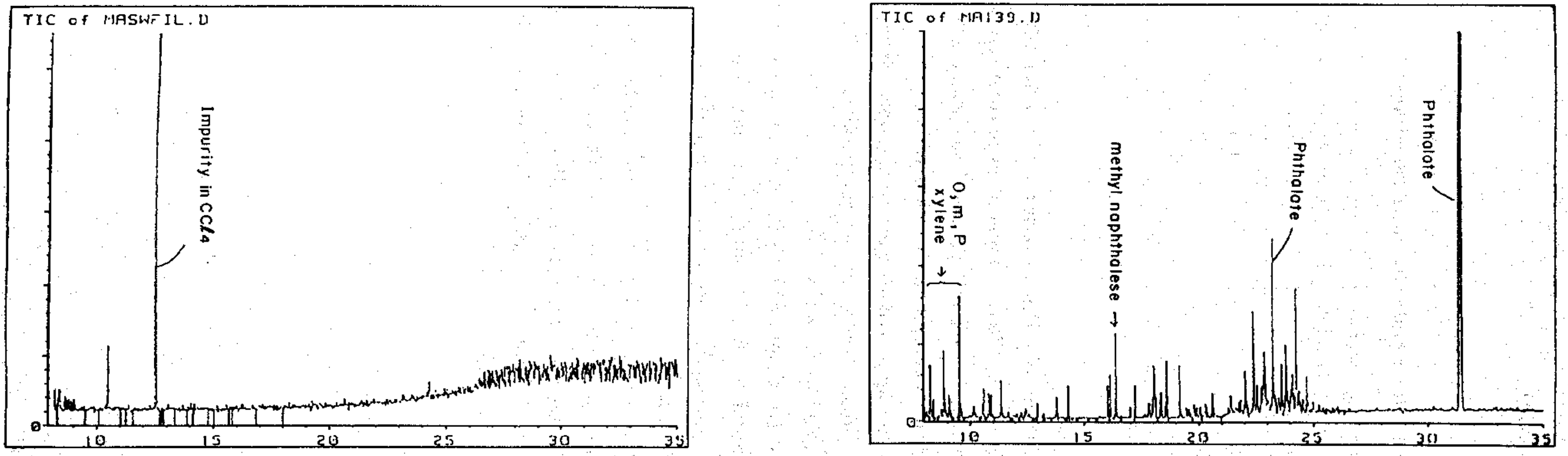
2) Component analysis of soluble oil

In Fig. 23, chromatography by GC-MS on oil-dispersed sea water, after filtration through a 0.2 μm pore diameter membrane filter, compared to normal sea water. It was confirmed that, most oil is removed from oil-dispersed sea water by using membrane filtration; however some components can not be removed.

By identification, only a few components appeared to exist, those were, xylene and methyl naphthalene which are low molecular aromatic compounds. This was because the absolute volume of the sample was not sufficient.

When the same experiment was conducted domestically with fuel oil A, components other than xylene and methyl naphthalene were found after filtration. These substances were trimethyl benzene, naphthalene, and dimethyl naphthalene. These were also found in this experiment (Fig. 23).

These are all low molecular aromatic compounds and the larger the number of carbon atoms in the structure the lower the solubility. However, Table 3 shows, the solubility of aromatic compounds is much greater than the paraffin series even if they share the same number of carbons. Therefore, the compounds detected in this experiment can be considered soluble compounds.



Sea water
(After membrane filtration)
Magnified

Oil-dispersed sea water
(After membrane filtration)
Magnified

Fig. 23 **GC–MS Chromatograph of Membrane Filtrate from oil dispersed in sea water (1) (continued)**

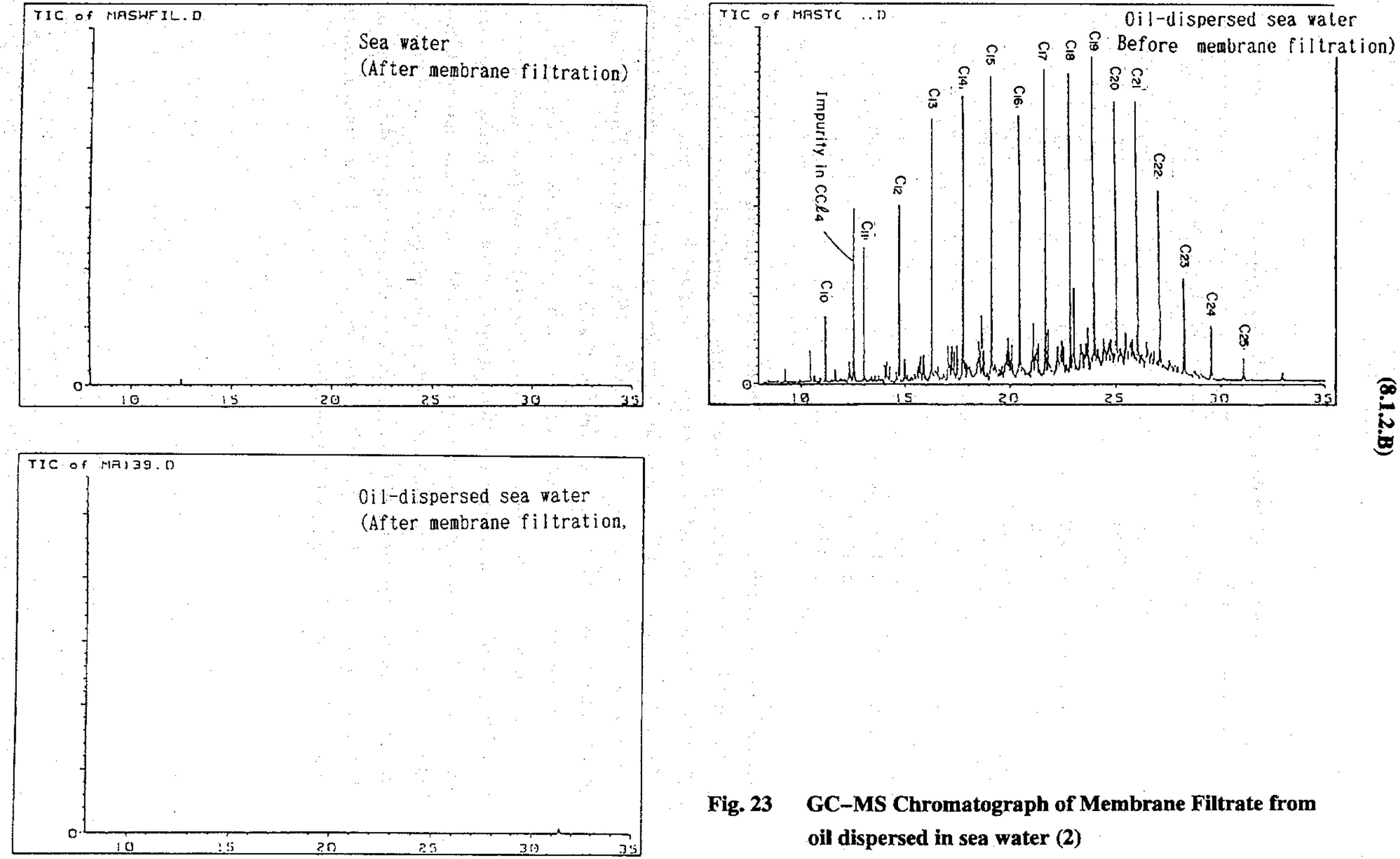


Fig. 23 GC–MS Chromatograph of Membrane Filtrate from oil dispersed in sea water (2)

Table 3 Solubility of some hydrocarbons[3,5]

	Chemical Compound	No. Carbon Atoms	Solubility [mg/l]
Aromatics	benzene	6	1780
	toluene	7	515
	xylene	8	175
	naphthalene	10	50
	phenantoren	14	1.07
	anthracene	14	0.075
	chrysene	18	0.002
Paraffin	methane	1	24
	n-hexane	6	9.5
	n-dodecane	12	0.0037
	n-octadecane	18	0.0021
	n-triacontane	30	0.002

3) Determining the abundancy ratio of soluble oil in oil-dispersed sea water.

By filtering the oil-dispersed sea water through the membrane filter selected for this experiment (assuming the oil in the filtrate was soluble oil) it become clear that the ratio of the oil content in the filtrate to the oil content in oil-dispersed sea water was nearly the same, approximately 10% (Table 4). This result was verified for the most part by the results in the domestic experiment.(Table 7)

Excepting that most of the soluble oil in sea water, which also exists in diesel oil, contains aromatics as mentioned in a preceding clause, the calibration curve for quantitative analysis was measured by florophotometry with the reference being diesel oil. The fluorescence intensity ratio of chrysene and other crude oils is shown in Table 5. This table shows that the ratios differ for each type of oil. In addition, the ratio for aromatic compounds like chrysene is significantly higher than in mixtures of hydrocarbons. Therefore, this oil, which we consider to be soluble, shows a comparatively high fluorescence intensity value.

Table 4 Filtration of oil-dispersed sea water with membrane filter

Oil [ppm]		After/Before filtration
Before filtration	After filtration	
6.1	0.6	0.10
6.3	0.4	0.06
7.6	0.8	0.11
8.1	0.6	0.07
8.7	1.0	0.11
Average		0.09

Table 5 Relative fluorescent intensity of crude oil compared to chrysene[3,6]

Oil (variety)	Fluorescent Intensity Ratio
chrysene	1.000
Iranian light crude	0.150
Arabian heavy crude	0.152
Oman crude	0.145
Minas (Sumatra) crude	0.140
Taching (China) crude	0.160
Fuel oil A	0.046

(Reference) Experiment Results in Japan

(1) Experimental Method

Apparatus and Reagents

Gas chromatography spectrometer
Fluorophotometer (Nihon bunko FP-770)
Microscope (Olympus BHS-PC-SW)
Ultrasonic cleaner (Branson B5200; 47khz, 120w)
Separating funnel (100ml)
Glass funnel
Separating funnel shaker (Iwaki KM-SHAKER, U-SN)
Filter-paper (Advantec 5A, φ 11cm)
Volumetric flask (25ml)
Erlenmeyer flask (1L)
Beaker
Pipet
Membrane filter (Milipoa, φ 47mm, Material: PTFE,
pore size: 1.0, 0.4, 0.2 μm)
Filter holder (Milipoa, for φ 47mm filter)
Syringe (50ml)
Sea water
Fuel oil A
Isooctane (Kanto Chemical, for fluorescent analysis)
Anhydrous sodium sulfate (Wako, special grade)

Oil content measuring method

Fluorophotometry

Procedure

1) Preparation of oil-dispersed sea water
Prepare oil-dispersed sea water according to Fig. 24

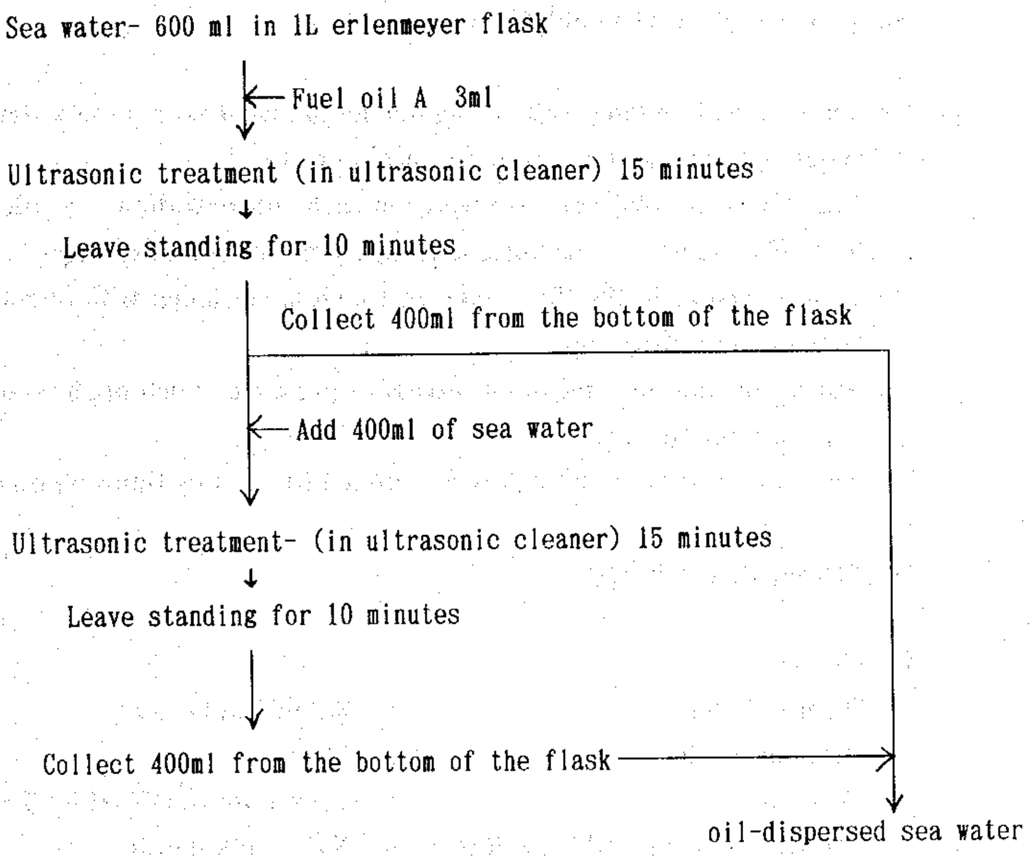


Fig. 24 Method for preparing oil–dispersed sea water

2) Selection of membrane filter

- **Prepare 10 ppm oil–dispersed sea water according to 1).**
- **Dilute above oil–dispersed sea water to each concentration. While shaking, collect 50 ml of sample from the bottom of the container with a syringe.**
- **Connect syringe to the filter housing which is equipped with membrane filter, and apply pressure filtration.**

  Observe precautions not to use excessive pressure which might result in forcing oil drops into the filtrate.

3) Analysis of soluble oil characteristics

The diameter of oil drops in dispersed sea water, prepared with the ultrasonic method were approximately 1 to 3 μm. This dispersion was filtered through a 0.2 μm pore diameter membrane filter. We consider the filtrate to contain soluble oil.

In this experiment we directly filtered oil–dispersed sea water through a 0.2 μm membrane filter, we used carbon tetrachloride in the extraction, and analyzed

components by a variety of GC methods.

4) Determine the abundance ratio of soluble oil in oil–dispersed sea water.
- Prepare oil–dispersed sea water according to 1).
- Dilute above oil–dispersed sea water to each concentration. While shaking, collect 50 ml of sample from the bottom of the container with a syringe.
- Connect syringe to the filter housing which is equipped with membrane filter, and apply pressure filtration.
  Observe precautions not to use excessive pressure which might result in forcing oil drops into the filtrate.
- Measure and compare oil before and after filtration by fluorophotometry.

GC measuring conditions

1) GC–D

Device Model : Shimadzu GC–9A
Detector Model : FID
Column Type : 1m x 2.6mm. OV–101 • 5 • 80/100 mesh
Carrier Gas Type and Flow Rate : N2 50ml/min
Oven Temp Program : 50 to 340℃
Oven Temp Program Rate : 10℃/min.

2) GC–AED

Detector Type : AED (Atomic Emission Detector)
Column Type : HP–1 (25m x O.2mm x 0.5 μm)
Oven Temp Program : 50℃ to 280℃
Oven Temp Program Rate : 10℃/min.
Carrier Gas Type : He
Split Ratio : 95 : 1

3) GC–MS (Quadruple Type MS)

Detector Type : MSD (Mass Selective Detector)
Column Type : DB–1 (30m x 0.25mm x 0.25 μm)
Oven Temp Program : 50℃ to 280℃
Oven Temp Program Rate : 10℃/min.
Carrier Gas Type : He

Split Ratio : 70 : 1

4) GC–MS (Magnetic Field Type MS)

Detector Type : MSD (Mass Selective Detector)
Column Type : DB–1 (30m x 0.25mm x 0.25 μm)
Oven Temp Program : 80℃ to 280℃
Oven Temp Program Rate : 8℃/min.
Carrier Gas Type : He
Split Ratio : 70 : 1

<u>Measuring Conditions</u>

Slit width : Excitation 10nm, fluorescence 10nm
Excitation wavelength : 310nm
Fluorescence wavelength : 343nm

(2) Experimental Results and Analysis

1) Selection of membrane filter

In Table 6, oil contents before and after filtration using membrane filters with three different pore sizes is shown. From these results, we found that there was not much difference in exiting oil by pore diameter, and that the three pore diameters can effectively filter out soluble oil from oil–dispersed water. However, when excessive pressure is used in the filtration process, there is a possibility for oil drops to form and go through the membrane. Therefore, we decided to use pore diameter 0.2 μm as the possibility of this occurring was considered to be lower if a smaller pores dimeter filter was used.

Table 6 Filtration of oil–dispersed sea water by membrane filter

Filter pore diameter [μm]	Oil before filtration [ppm]	Oil after filtration [ppm]
1.0	1.1	0.2
0.4	1.1	0.2
0.2	1.1	0.1

2) **Component analysis of soluble oil**

We found a marked difference, as shown in Fig. 25, when comparing the distribution of components before and after filtration. It was also found that some substances peaked at low bowling points.

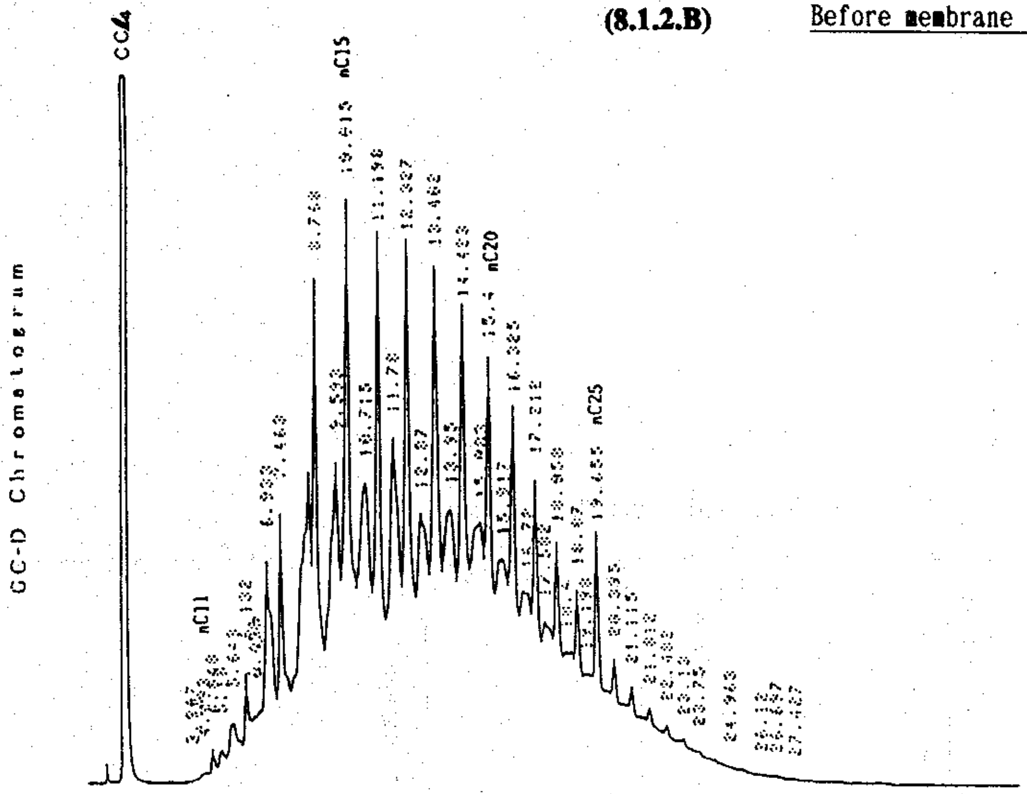
As a result of analyzing oil components in these filtrates, it became clear that the majority of the components were from the naphthalene series. The boiling point range for these was about 220 to 260 °C, which is also about the same as fuel oil A. These were not found in the original sea water sample, so it was assumed that they were from fuel oil A.

The solubility of naphthalene is not very high at 50ppm, but slight amounts of these compounds were detected.

These components are soluble in sea water and can not be removed by direct filtration. From results of the GC-AED the unknown component in Fig. 26 was found to contain oxygen and it was determined to be an ester with a molar weight of 284. Following results of the GC-MS determined that is was $C_{18}H_{28}O_4$, however the structure could not be confirmed. This component could be ester phthalate a contaminant which entered during the experimental procedure (Fig. 27, 28).

(8.1.2.B)

Before membrane filtration



After membrane filtration

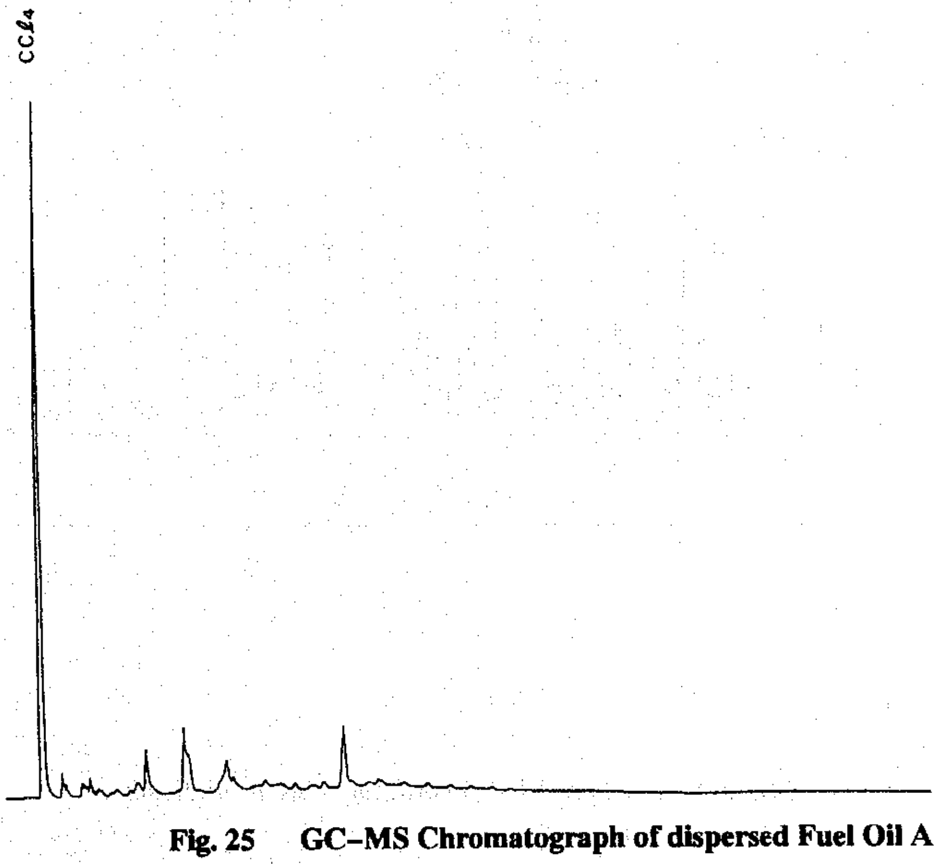


Fig. 25 GC–MS Chromatograph of dispersed Fuel Oil A (2)

(8.1.2.B)

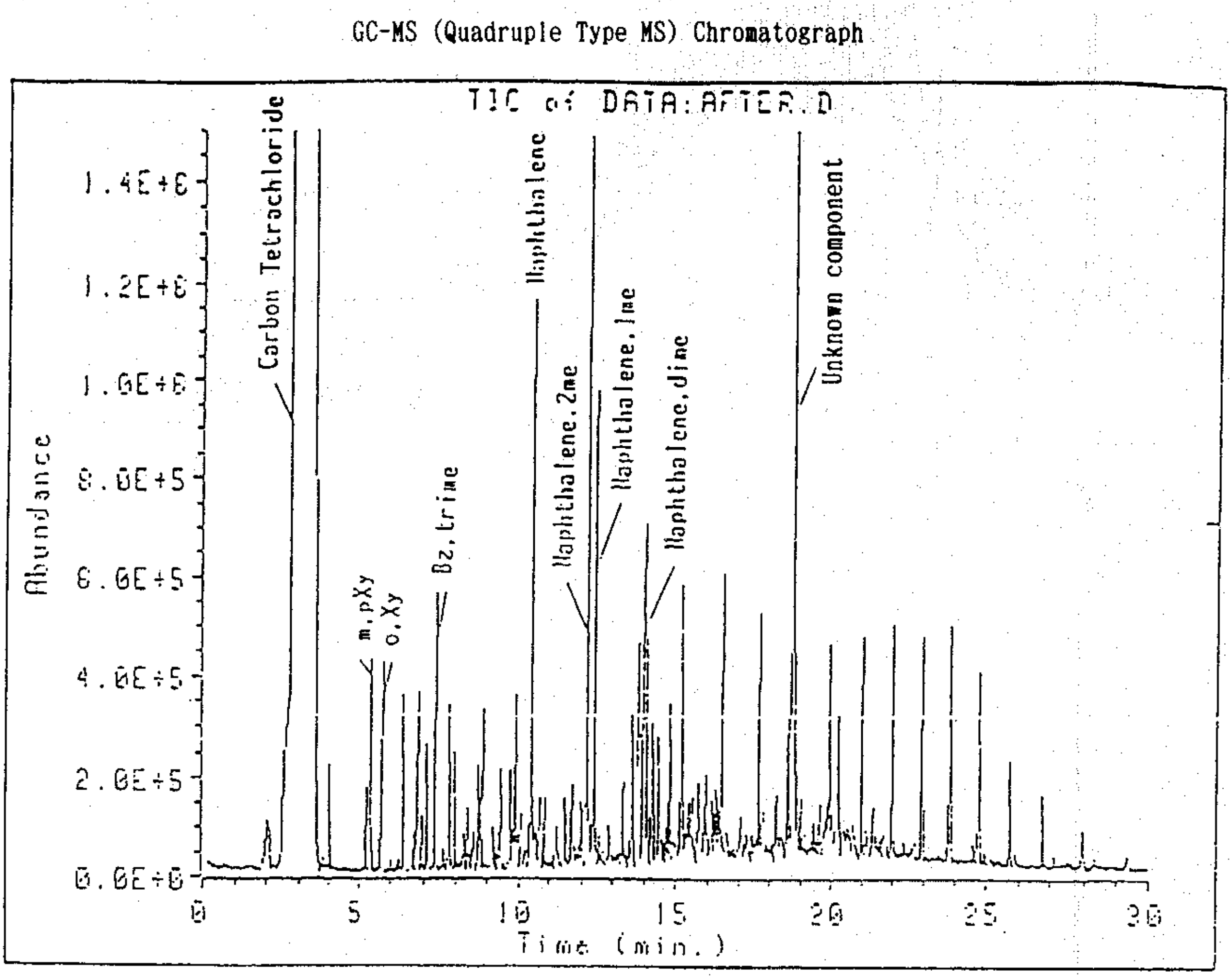


Fig. 26 GC–MS (Quadruple Type MS) chromatograph of oil dispersed in sea water after filtration

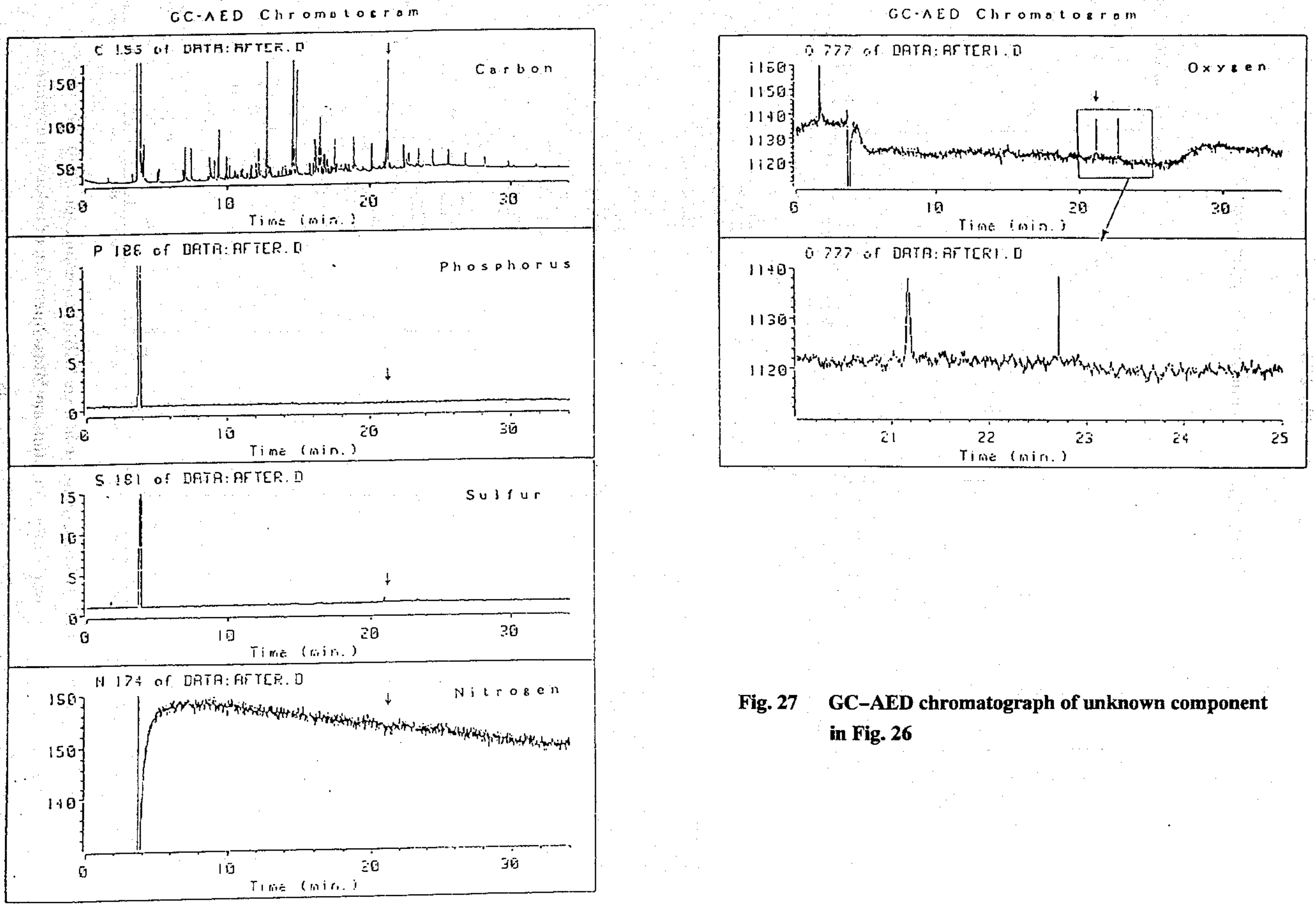
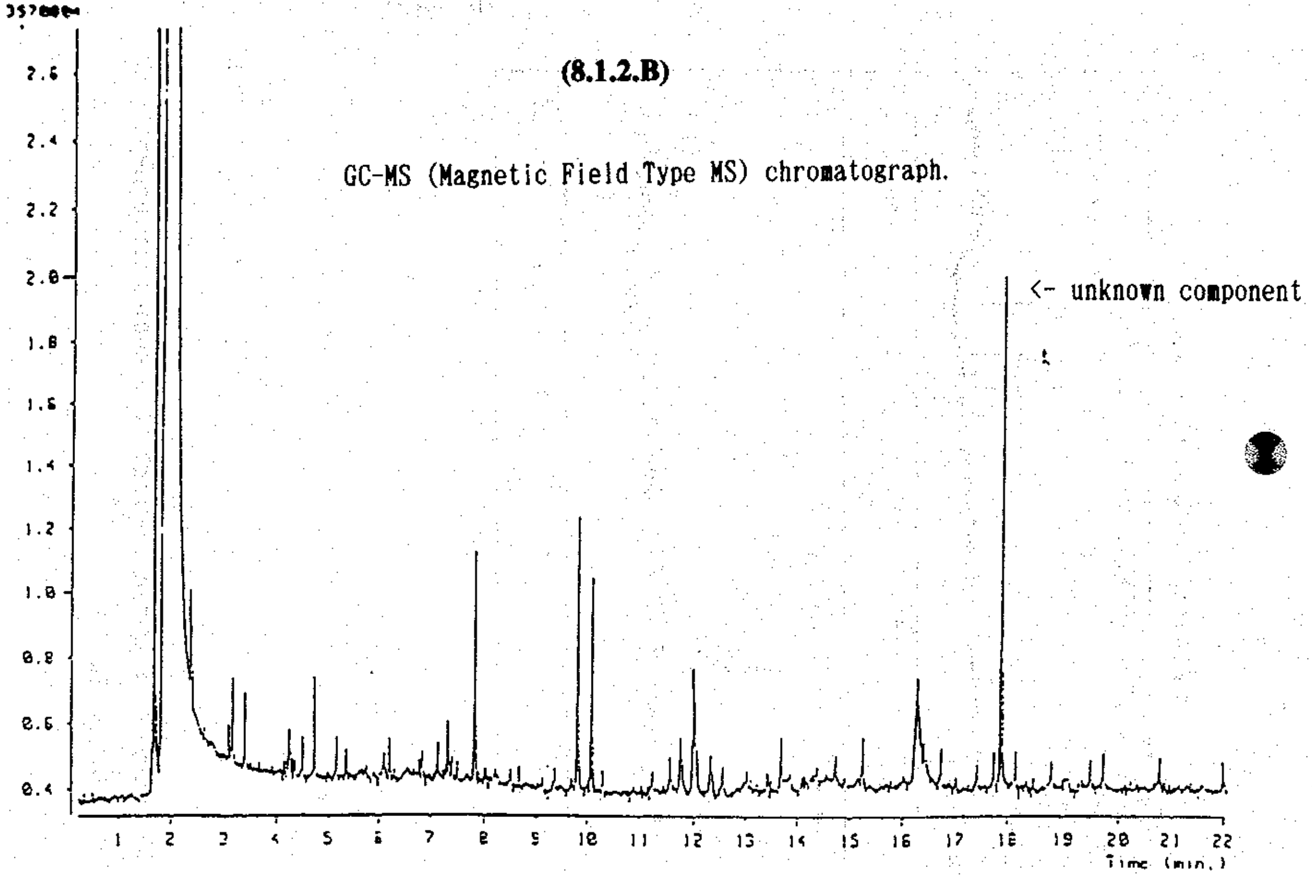


Fig. 27 GC–AED chromatograph of unknown component in Fig. 26

(8.1.2.B)



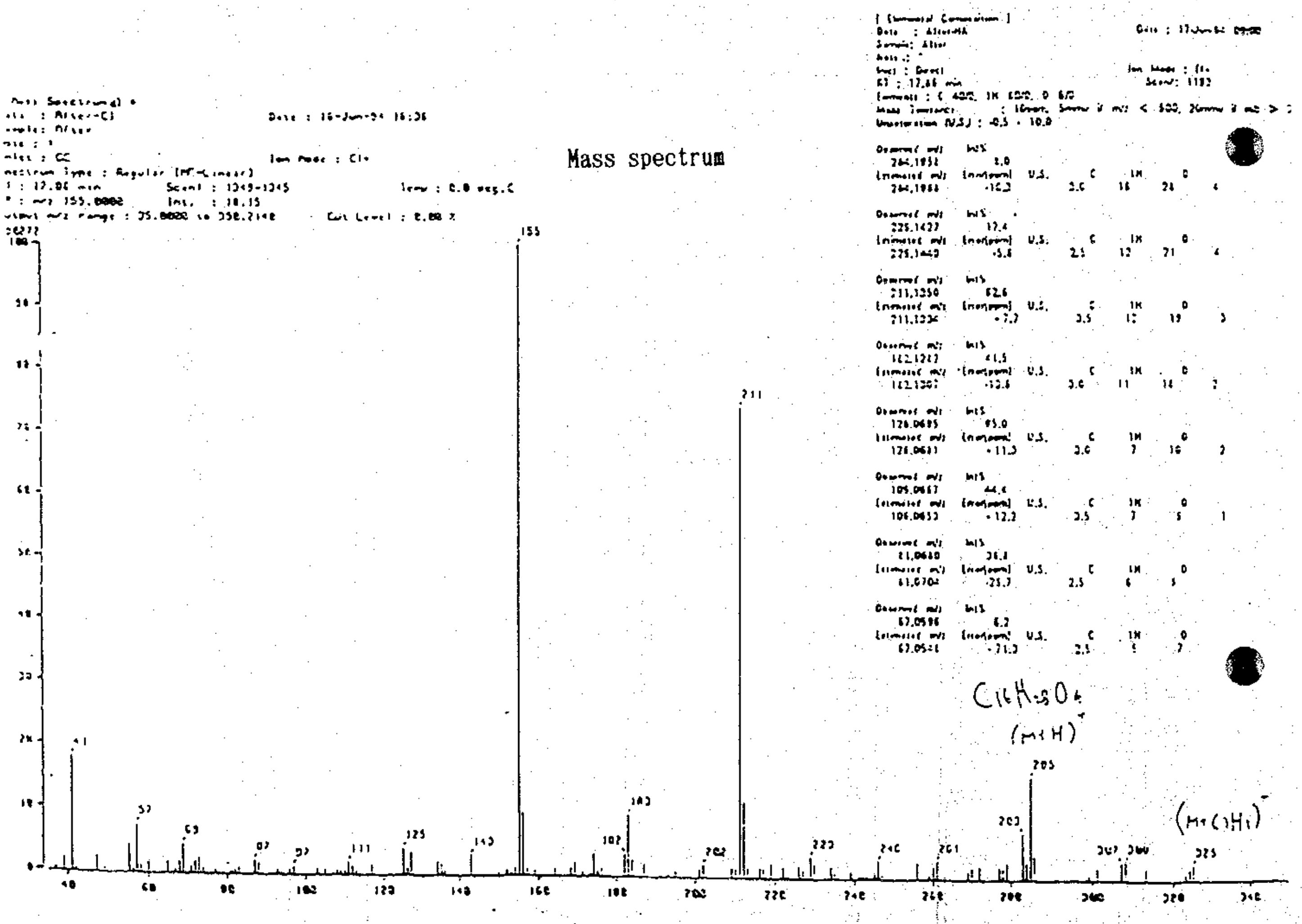


Fig. 28 GC–MS (Magnetic Field Type MS) chromatograph of oil–dispersed sea water after filtration and Mass Spectrum of unknown component.

3) Determining the abundance ratio of soluble oil in oil–dispersed sea water

Oil concentrations before and after filtration are shown in Table 7. The concentration of oil in the filtrate is consistent with the concentration before filtration, about 10% of the original concentration. This indicates that certain portions of dispersed fuel oil A are soluble oil.

Further, because the fluorescent method, which was one of our oil measuring methods, measures fluorescence readily emanated by aromatics, it would measure higher than the actual oil in the case that the sample contained many aromatics. Actual oil would be lower than this.

Table 7 Oil concentrations before and after membrane filtration of oil–dispersed sea water

Oil [ppm])		After/Before filtration
Before filtration	After filtration	
1.1	0.1	0.09
5.2	0.6	0.12
7.0	0.7	0.10
59.0	3.7	0.06
Average		0.09

5. Study of filter materials' resurgent back washing (determination of back washing flow rate)

(1) Objectives

To determine the optimum back washing flow rate and filter material to evaluate its resurgent capacity.

(2) Experimental method

Apparatus and Reagents

Oil obsorbing and removing equipment
Sand (0.6mm)
Anthracite (1.0mm)
Polymer (Chemceptor CM 121, 1.0mm)

Procedure

- Put varieties of filter materials (including activated charcoal) into the filter column in oil absorbing and removing equipment.
- Let tap water run down into the filter column for each LV rate.
- Measure the height of filter materials in the part where developed and find the relation between LV and the percentage of development.

(3) Results

The optimum percentage of development for the filter layer depends on the void ratio (ε) of the filter materials before back washing. The optimum percentage of development is shown in the following formula;

$$\text{Optimum percentage of development} = (0.6 - \varepsilon)/0.4 \times 100$$

Table 8 shows the LV rates for each filter material based by calculating the optimum percentage of development from the void ratio of each filter material. If resurging of filter materials by back washing is desired, do back washing with LVs shown below. Except when the temperature of water deviates from 20 $^{\circ}$C, it must be multiplied by the figures shown in Table 3.8.

Table 8 **The optimum percentage of development for each filter material and LVs**

Filter material	Optimum percentage of development [%]	LV [m/hr]
Sand	30	50
Anthracite	30	30
Polymer	30	10

Table 9 **Temperature of water and multiplier figures for back washing**

Temperature of water (°C)	Multiplier figures
10	0.91
20	1.0
30	1.08
40	1.15

6. Conclusion

1) As a result of each examination, it was confirmed that the direct filtration method using ferric chloride is the most generally effective procedure for pre-treatment. In beaker scale experiments, it was also confirmed that any filter materials can remove oil satisfactory.

2) In bench scale, the floc which was formed by adding flocculants is physically very fragile, and the time before deterioration is very short as it can be destroyed by pumped water alone. By using an empty column as an agglutination column, it increases floc and makes effective direct filtration possible.

3) In the case of filtering oil-dispersed sea water with membrane filters, compared to prior to filtration extremely small components remain in the filtrate. Also the before and after distribution of the components changes. The majority of the components after filtration are aromatic compounds and are considered to be soluble substances from their molar weight and structure. These were determined to account for the very small amount of soluble oil which exists in oil-dispersed sea water and were fractionated by membrane filters.

7. References

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(2) "Technology and Apparatus for Water Pollution Prevention" Sancho Shuppan

(3) Hassan, Ata M. et al, "Performance Evaluation of SWCC SWRO Plants Part II", SWCC Research Activities and Studies, 2, 94-121, 1991

(4) Kitakawa, M. et al, "Results of Flocculants for Removing Oil from Raw sea water", Japan International Cooperation Agency, Saudi Arabia, Cooperative Desalination Technology Study Reports, 1982

(5) Mayan Kutty, P.C. et al, "Monitoring of Oil Spill Contaminants in Water Samples from SWCC Desalination Plants at Al-Jubail and Al-Khobar", SWCC Research Activities and Studies, 2, 156-181, 1991

(6) Yoshimura, H., "Oceanic Oil Pollution and Analytical Methods", Environment and Mensuration Technology, 14 [11], 47-58, 1987

8.1.2.C. Analysis of Trihalomethane and Formation of Trihalomethane

(8.1.2.C)

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Chlorine is injected to prevent the blocking of the intake of sea water desalination plants with the adherence of shellfish in the vicinity of the intake. However, the chlorine may cause a chemical reaction of certain types of organic matter in the sea water, forming trihalomethane, a carcinogenic substance. Using such sea water in the untreated state in a sea water desalination plant may cause a problem. This document examines the formation and elimination of trihalomethane in oil–polluted sea water.

1. Formation of Trihalomethane in Oil–polluted Sea Water

1.1 Background and Purpose

It is already known that trihalomethane (THM) is formed when sea water taken into a sea water desalination plant is chlorinated. It is interesting to see what changes occur when sea water polluted with oil is treated with chlorine. Here we made a study of the formation of THM when oil–diffused sea water was chlorinated.

1.2 Experimental Method

Apparatus and Reagents

GC–ECD analyzer
TOC analysis gauge (Shimazu TOC–500)
Ultrasonic washer (Blackstone HT–1.9, 5A, 0.6kVA)
Beaker
Pipette
Conical flask (1 L)
Fuel oil 'A'
Sea water

Analytical Methods

Oil content measuring method : TOC method
THM analytical method : Purge trap method

THM Analysis Conditions;

Analyzer : HP–5880 (with 63Ni EC detector)
Purge trap auto injector : Tekmer Model LSC–2
Adsorption column : Tenax column

Separation column : Fused silica capillary column
DB5 (30m x 0.5mm/id)
Quantity of sample volume : 5 ml
Temperature of adsorption : 180℃
Carrier gas : He
Make–up gas : N2
Temperature of injector : 200℃
Temperature of detector : 250℃
Gradient of column temperature : 1) Initial : 40℃, 3 min.
2) Gradient : 8℃/min.
3) Finishing : 150℃

THM Reaction Conditions

Reaction temperature : Room temperature
Reaction illuminance : Laboratory lighting

Procedure

1) Preparation of oil–dispersed sea water

Oil–dispersed sea water was prepared by the procedure shown in Fig. 1.

Sea Water 1 L (using 1 L conical flask)
↓ ← Fuel oil 'A' 5 ml
Ultrasonic treatment (ultrasonic washer) 20 minutes
↓
Leave standing for 10 minutes
↓
Collect 650 ml from bottom of receptacle
↓
Leave standing for 60 minutes
↓
Measure TOC
↓
Dilute with sea water (approx. 1–10 ppm)

Fig. 1 Method of Preparing Oil–Depersed Sea Water

2) THM Forming Reaction

At an actual plant, about 10 minutes is required to reach the desalination step after water is taken in and disinfected with chlorine. Because of this, we had initially scheduled the reaction time for 10 minutes after chlorination, however, results of preliminary study showed that the time was too short as there was practically no consumption of chlorine in the reaction time of 10 minutes. Accordingly, we decided to check the formation of THM by making the reaction time longer. For this, we made two types of oil-dispersed sea water of concentrations of approximately 1-10 ppm, one with an initial chlorine additive of low concentration (1.6 ppm) and the other of high concentration (9 ppm).

NaOCl (1.6 ppm and 9 ppm) was added to the oil-dispersed sea water prepared as in 1) above, and chlorine reaction allowed to take place (for 96 hours). At this time, the reaction liquid was kept away from contact with air by filling it in a glass container (capacity 70 ml).

The reaction liquid was collected by the purge trap method and THM analyzed with the GC-ECD.

1.3 Results and Comments

Fig. 2 and Fig. 3 show THM formed in each of the two chlorine concentrations. In all test samples, the concentration of $CHBr_3$, the final substance formed in the series of THM formation reactions, was the highest among the various trihalomethanes.

In each test sample, the quantities of the respective THM compositions changed together with the reaction time, showing that the formation of THM is a chain reaction*. Moreover, there was a tendency for the THMs in each test sample to increase as higher the oil content of the sea water and longer the reaction time. The following causes are supposed for this reaction: There is a higher content of organic substances that reacted with the chlorine as higher the oil content in the sea water, and the formation of THM increased the longer the reaction time.

Furthermore, the formation of $CHBr_3$ ceased once there was no more residual chlorine (in Fig. 2, the concentration of the residual chlorine after 24 hours, when the initial oil content in the samples was 3.3, 6.0 and 10.4 ppm, was respectively 0.18 ppm, ND and ND, after which the concentration of $CHBr_3$ became more or less constant). On the other hand, in Fig. 3, the concentration of the residual chlorine in the samples after 48 hours, when the initial oil

content in the samples was 2.4, 4.5 and 12.6 ppm, was respectively 4.1, 4.0 and 3.0 ppm and the formation of $CHBr_3$ increased together with the reaction time.

Note that in some of the samples, the $CHBr_3$ concentration decreased despite the fact that the reaction time became longer, but this is believed to be caused by some of the $CHBr_3$ evaporating during the time measurements were being made.

*** : Sequence of THM formation:**
$CHCl_3 \rightarrow HCl_2Br \rightarrow CHClBr_2 \rightarrow CHBr_3$
The finally formed substance, $CHBr_3$, is extremely stable.

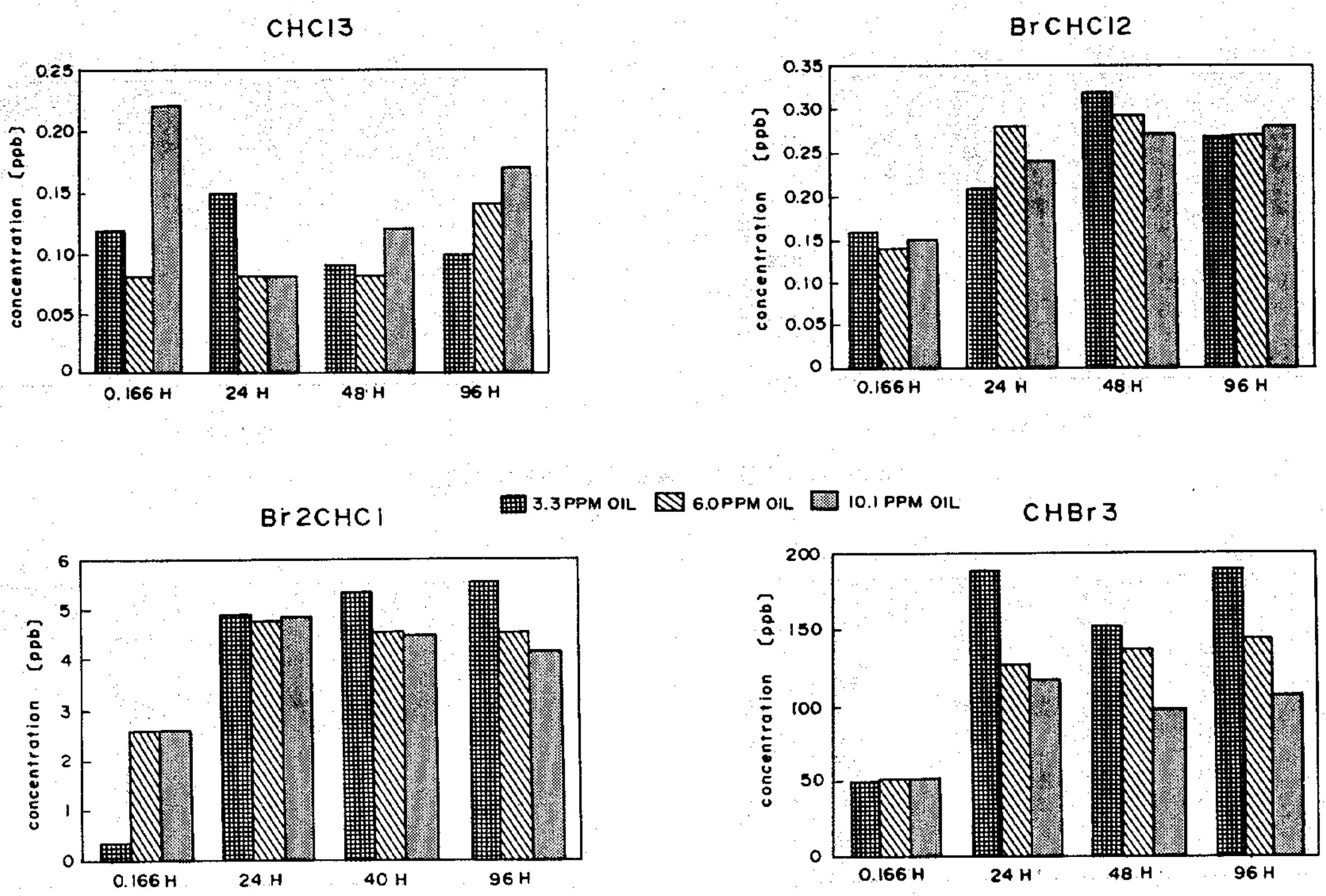

Fig. 2 THMS formation under low chlorination (1.6ppm)

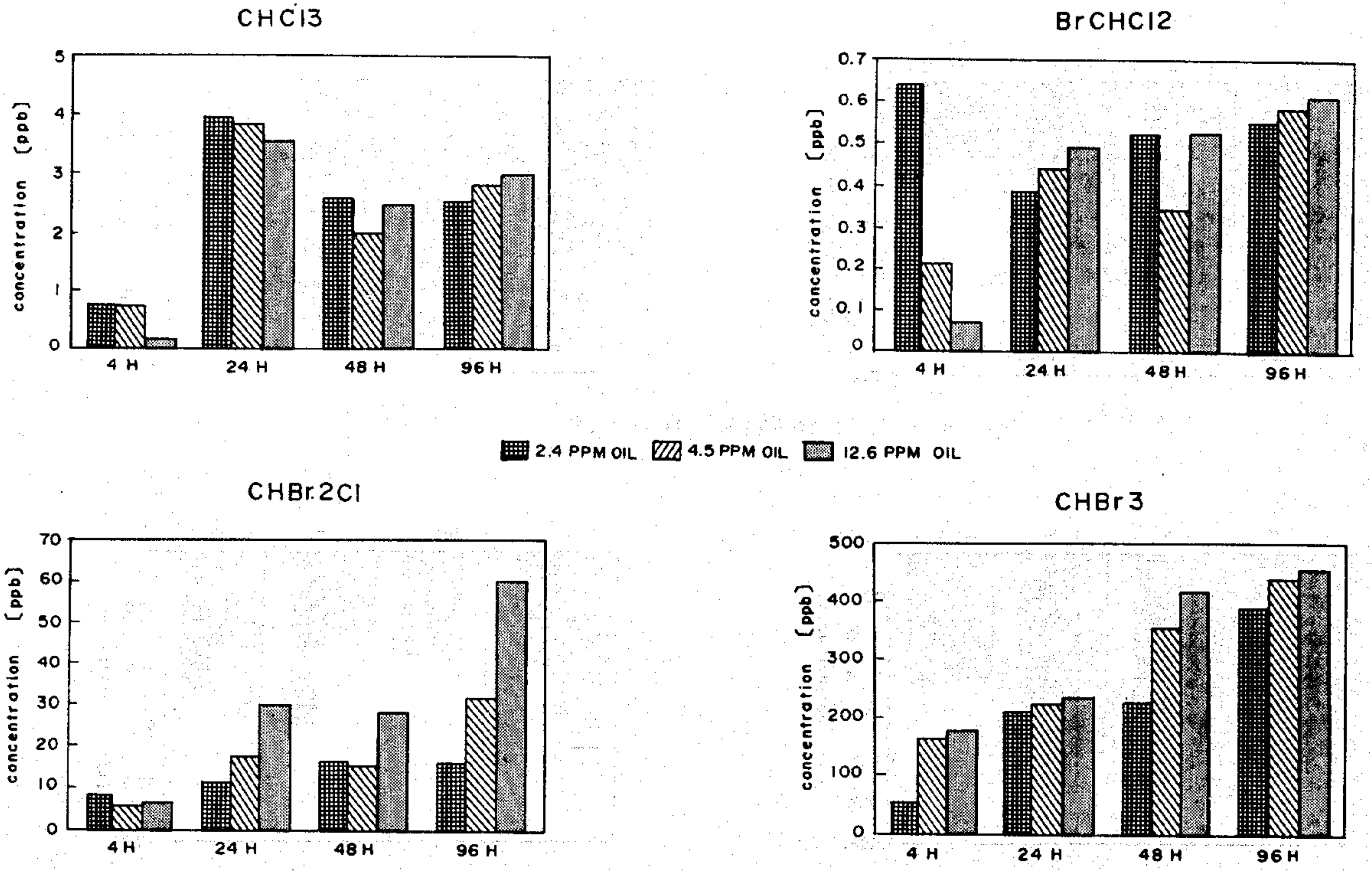

Fig. 3 THMS formation under high chlorination (9.0ppm)

2. Effect of Oil Content Removal Treatment to Reduce the Formation of Trihalomethane

2.1 Objectives

When oil removal treatment including activated carbon treatment is conducted on oil-dispersed sea water, even the soluble oil content is removed by the activated carbon, it is expected that the amount of trihalomethane formed in oil-dispersed sea water after oil removal treatment (after activated carbon treatment) will decrease compared to the case where the removal treatment has not been conducted. In order to verify this, we investigated the formation of trihalomethane in samples of oil-dispersed sea water which had been subjected to oil removal treatment.

2.2 Experimental Method

Apparatus and Reagents

GC-ECD analyzer
TOC analysis gauge (Shimazu TOC-500)
Ultrasonic homogenizer (Ultrasonic Engineering USH-300Z205)
Peristaltic pump (Tokyo Rikakiki RP-1000)
Glass column (Shibata Kagaku HLC-20S: ϕ 2 cm, L = 30 cm)
Beaker
Pipette
Conical flask (1 L)
Silicon tube
Fuel oil 'A'
Sea water
Sand (0.6 mm)
Anthracite (1.0 mm)
High polymer filter medium (Chemceptor CM 121, 1.0 mm)
Ferric chloride (Fisher, Anhydrous purified grade)

Analytical Methods

Oil content measuring method : TOC method
THM analytical method : Purge trap method

(8.1.2.C)

THM Analysis Conditions:

Analyzer : HP-5880 (with 63Ni EC detector)
Purge trap auto injector : Tekmer Model LSC-2
Adsorption column : Tenax column
Separation column : Spelco, Vocol, Fused silica, 30 m
Quantity of sample volume : 5 ml
Temperature of adsorption : 180℃
Carrier gas : He
Make-up gas : N2
Temperature of injector : 200℃
Temperature of detector : 250℃
Gradient of column temperature : 1) Initial : 33℃, 3 min.
2) Gradient : 4℃/min.
3) Finishing : 150℃

THM Reaction Conditions

Reaction temperature : Room temperature
Reaction illuminance : Laboratory lighting

Procedure

1) Preparation of oil-dispersed sea water

- While circulating 1 L of sea water inside the ultrasonic homogenizer with the peristaltic pump, 2.5 ml of fuel oil 'A' was injected into the silicon tube in which the sea water was circulating, and then, in that state, subjected to 10 minutes of ultrasonic treatment.
- The rich oil-dispersed water thus obtained was adjusted to the oil content concentrations to be tested by diluting with sea water.

2) Preparation of samples

- 3 ppm of ferric chloride was added to the diluted oil-dispersed sea water, which was then subjected to 1 minute of rapid agitation (of about 100 rpm) and then to 30 minutes of slow agitation (of about 40 rpm).
- The above sample water, while being agitated slowly, was pumped by the peristaltic pump through glass columns connected in series and filled with each type of absorbent, and samples were collected from the inlets and outlets of the columns.

- Together with measuring the oil concentration in the collected samples, NAOCl (9 ppm) was added and chlorine reaction was made to take place (for 72 hours). At this time, the reaction liquid was kept away from contact with air by filling it in a glass container (capacity 70 ml).
- The reaction liquid was collected by the purge trap method and THM analyzed with the GC-ECD.

Oil Removal Treatment Conditions

Column size	:	ϕ 2 cm, L = 30 cm
Filter media	:	1st stage: High polymer, 2nd stage: Sand, 3rd stage: Activated carbon
Filter media height	:	20 cm
Flow rate of water	:	3.1 L/hr. (LV 10 m/hr., SV 50 m/hr.)

2.3 Test Results

Oil concentrations after each treatment are shown in Table 1 and the respective formation of trihalomethane in Fig.4.

Practically all the oil content was removed by the high polymer column, and analysis by GC-MS, conducted as a double-check in addition to the TOC method, showed the oil concentration to be below the detectable limit (about 1 ppm) (Table 1).

Table 1 Oil Content at Each Pretreatment Stage

	Oil Content [ppm]	
	TOC	GC-MS
oil-dispersed sea water	27.7	30.3
After high polymer	1.2	Nil
After sand filtration	0.5	Nil
After activated carbon	0.3	Nil

After the activated carbon treatment, the amount of bromoform formed by reacting with chlorine for reaction time of 24 hours or more was less than in the case of other samples. Also, while the quantity of bromoform formed in sea water after 10 minutes of reaction time was less than that formed respectively in oil-dispersed sea water, after high polymer, and after sand filtration, it was practically the same in the case of reaction time of 24 hours or more (Fig.4).

Almost all oil content was removed by coagulating filtration, and, finally by activated carbon treatment, it is believed that not only the soluble oil content but such THM precursors as the humin matter in sea water were also removed, and the amount of THM (mainly bromoform) formed in each sample was expected to be as follows:

After activated carbon < sea water < after sand filtration ≧ after high polymer << oil-dispersed sea water

However, the results of this experiment did not completely coincide with that.

In the results of "1.1 Formation of Trihalomethane in Oil-Polluted sea water" the amount of trihalomethane formed in oil-dispersed sea water increased together with the duration of reacting with chlorine, and, after 96 hours, became more than 400 ppb. For this time however, subsequent to 24 hours, no tendency could be seen for the formed amount to increase in keeping with the reaction time, maintaining practically the same level (about 120 ppb) as in the case where only sea water was involved (Fig.5). From the analysis results (Fig.5) showing that the oil component distribution of the fuel oil 'A' used this time of experiment had shifted more to the high molecular side than in the previously-used fuel oil 'A', it is supposed that this sort of result was obtained possibly because there was less of the components of small molecular weight that are apt to be attacked by chlorine.

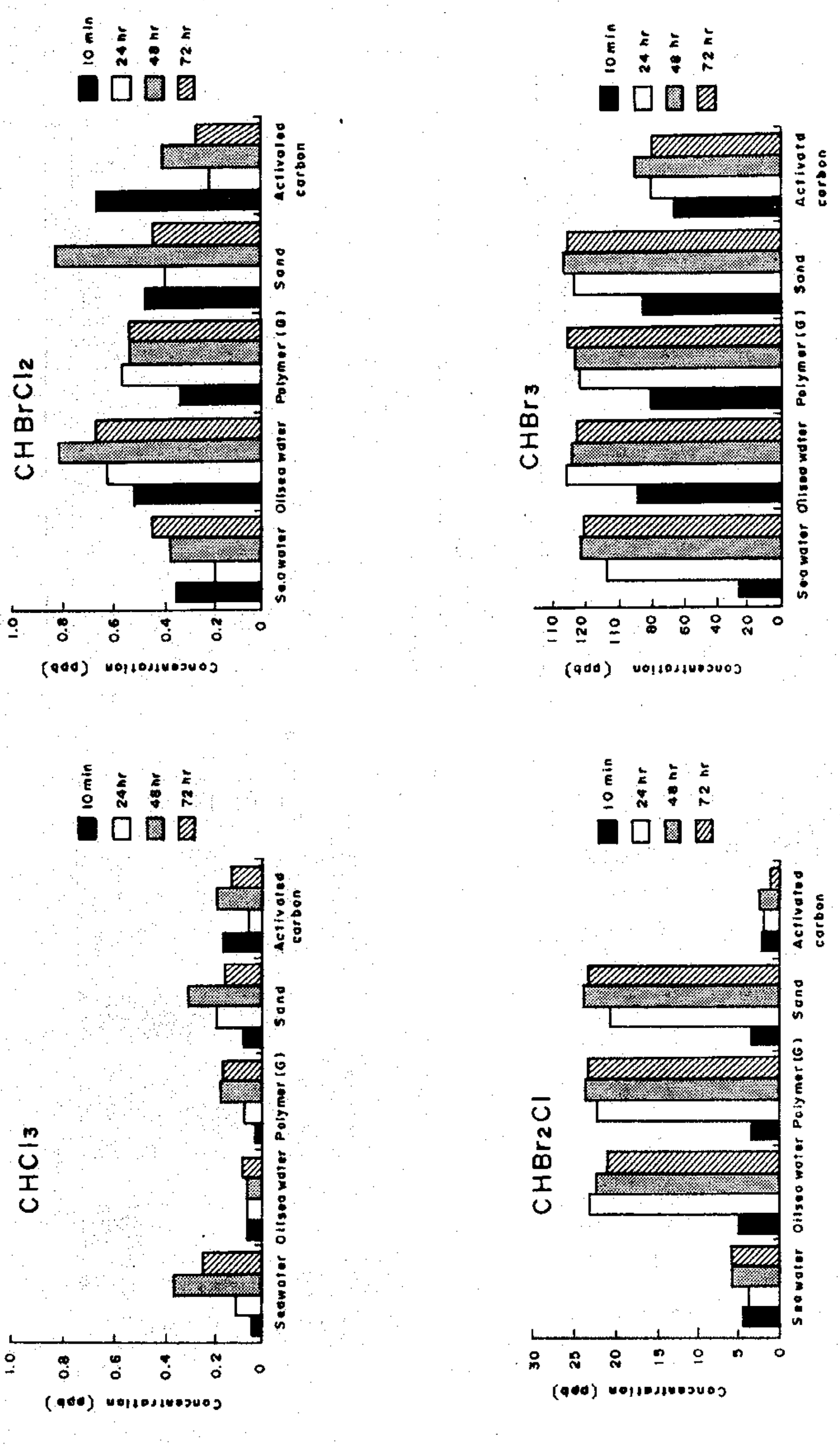

Fig. 4 Trihalomethane formation on each step sample of oil removal

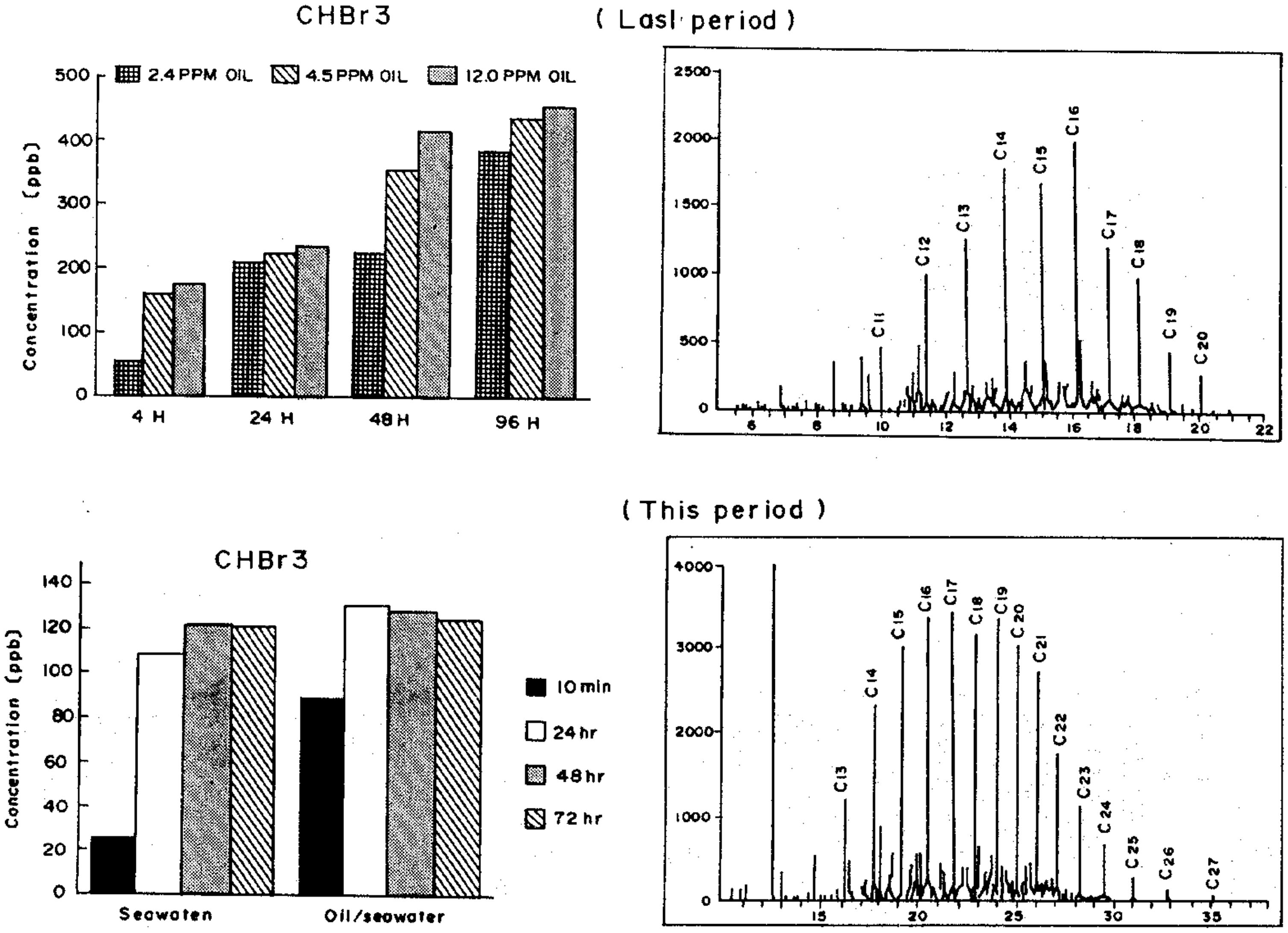

Fig. 5 Rerationship between oil componenl distribution and CHB_{13} formation