

**8. Study on Countermeasures against Oil Contamination
for RO Process (RO-2)**

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8. Study on Counter measures against Oil Contamination

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9. Summary

Pollution of seawater in the Arabian Gulf has advanced steadily in recent years, in particular oil pollution of the sea by petroleum outflows during the Gulf War has become a serious problem. Oil has a general tendency to adhere to solid surfaces and in the case of water such as seawater, which contains salt, this tendency is particularly strong with small quantities of oil forming a thin covering over a wide solid surface. Also, the reverse osmosis separation function uses extremely thin film surfaces so that a small quantity of oil covering the membrane surface could cause a remarkable deterioration in the separation function. With normal RO desalination equipment, the seawater is pretreated by coagulation and sand filtration but the current practice is that the operation must be suspended if oil is mixed with the intake water, so that with the recent increase in oil pollution, a method is being sought for safe operation even when the seawater is mixed with oil. Oil in seawater is either dispersed as an emulsion in the water or dissolved in the water but the majority of the oil is in the former condition, the amount in solution being comparatively small. Consequently, it is considered that most of the oil in the seawater may be removed by using coagulation and sand filtration to remove the oil emulsion which constitutes the major part of the oil content in the seawater.

The present study involves, conducting a literature survey on oil and THM in seawater, establishing an already available analytical method for the analysis of oil and THM obtaining best method for removal of oil from oil contaminated seawater and evaluating the effect of pretreated oil contaminated seawater on SWRO membrane.

8.1 Investigation and Preparative Experiment

8.1.1 Literature Survey

8.1.1.A. Oil and Trihalomethane in Seawater

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1. Objectives

To collect literature and information concerning oil and trihalomethane in the ocean and their separation methods. These materials may cause a problems. In the operation of RO seawater desalination plant. THM is carcinogenic agent and is known to cause cancer.

2. Method of Investigation

Information retrieval survey concerning oil, trihalomethane and organic matter dissolved in the ocean seawater was conducted using Japanese information retrieval system JOIS.

3. Results of Survey

The following is a summary of the literature survey.

(1) Oil content in seawater

There are extremely few articles concerning the oil content of seawater. Table 1 introduces an example of a report of an investigation of the distribution of oil concentrations near a marine oil field

After 50 hours from stopping the oil extraction, the maximum oil concentrations of 0.13 to 0.24 ppm were detected at a point 5 nautical miles (9 km) distant from the point of extraction. Also, 20 nautical miles (37 km) away, the concentration had fallen to the background level (0.07 ppm). According to another paper, nearly all measurements of the oil content in the sea near Japan are below 10mg/l and there is no noticeable difference in marine life between the marine areas. The results of oil measurements in the major bays of Japan show that all the maximum, minimum and mean values for all bay "seawater" in the maritime areas of Japan and its environs have similar levels.

(2) Trihalomethane in Seawater

Literature related to the measurement of trihalomethane in the oceans is extremely scarce. One paper which investigates the formation of trihalomethane (THM) by the addition of chlorine during the desalination of Arabian Gulf seawater¹⁾. The Water and Electricity Department of the Emirate of Abu Dhabi conducted basic experiments to study the formation of THM in plants producing fresh water by the distillation of Arabian Gulf seawater. According to this, if the seawater is normal and natural

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seawater, the formation of THM in plants producing fresh water by distillation is maintained within government and international standards. However, it concludes that, if the sea is polluted by the outflow of crude oil, etc., it is necessary to suppress the formation of THM by reducing the level of chlorination and to monitor the formation of THM by increasing the distilled water sampling frequency.

Second paper reports instances of , high concentrations of THM as chloroform in Japanese seawater in Kobe Port (492 ppb), off Takasago (1149 ppb), off Himeji (507 ppb), etc. and low concentrations of 3 to 250 ppt inside Osaka Bay. The results obtained by Okamoto et al inside Osaka Bay are shown in Table 2. These results are reported to be ten to one hundred times higher than the results obtained in the same year in surveys by Okamoto et al in Suo Nada and Hiuchi Nada in the Seto Inland Sea²⁾.

Considering that since both the solubility and vapor pressure of THM components are high, dispersion in both the hydrosphere and atmosphere will be rapid and it is extremely unlikely that high concentrations of THM would exist offshore. Therefore, it is conceivable that concentrations will range between several tens and several hundreds of parts per trillion as shown by Okamoto et al.

- 1) D. Cormack: "Response to Oil and Chemical Marine Pollution", Applied Science Publishers Ltd.
- 2) Hydrographic Department, Maritime Safety Agency: Marine Pollution Survey Reports, No. 19, March, 1993

(8.1.1.A)

Table 1 Concentration of Oil in the Seawater in the Ekofisk Oil Field

Distance and direction from rig	Depth (m)	Concentration (ppm)
3 n.m. N, thin sheen	1	0.118
3 n.m. N, thin sheen	2	0.135
3 n.m. N, thin sheen	4	0.121
5 n.m. N, thin sheen	1	0.245
5 n.m. N, thin sheen	2	0.133
5 n.m. N, thin sheen	4	0.133
10 n.m. N, thin sheen	1	0.089
10 n.m. N, thin sheen	2	—
10 n.m. N, thin sheen	4	0.040
15 n.m. N, sheen windrows	1	0.055
15 n.m. N, sheen windrows	2	0.055
15 n.m. N, sheen windrows	4	0.044
15 n.m. N, 3 n.m. W, flecks of w/o emulsion	1	0.053
	2	0.061
	4	0.043
15 n.m. N, 3 n.m. W, flecks of w/o emulsion	1	0.033
	2	0.019
	4	0.038
20 n.m. N	1	0.005
No visible sheen	2	0.011
No visible sheen	4	0.028

*Reference: D. Cormack: Response to oil and chemical marine pollution, Applied Science Publishers Ltd.

(8.1.1.A)

Table 2 Concentration of Halogenated Organic Materials in the Seawater within Osaka

St. NO#	CCl ₄	CHCl ₃	CHCl =CCl ₂	CCl ₂ =CCl ₂	CH ₂ Cl -CH ₂ Cl	Salinity (%)
St. 1	50	250	1200	730	3600	20.1
2-S	30	160	290	390	2000	21.1
2-B	3.7	10	31	50	87	32.3
3	49	180	240	290	770	27.1
4	22	15	130	210	550	24.6
5	13	51	94	150	1600	27.8
6	12	23	72	110	3500	30.5
7-S	14	23	150	140	1900	29.1
7-B	1.9	3.4	13	13	36	33.4
8-S	12	81	82	100	800	30.2
8-B	2.6	5.2	14	20	27	33.4
9	21	27	170	160	230	30.9
10	19	41	130	130	90	29.8
11	70	14	53	61	270	31.6
12	23	50	41	42	130	30.7
13	9.4	27	36	33	120	31.8
14	2.5	12	27	34	100	32.5
15	5.2	16	39	43	260	30.7
16-S	36	20	67	88	470	30.2
16-M	2.1	32	29	9.8	46	33.6
16-B	1.5	11	10	11	41	34.0
17	4.8	13	41	42	160	31.4
18	1.8	14	51	23	44	32.9
19	1.0	57	30	18	41	31.8
20	1.0	45	13	32	31	31.8

*S:Surface M:Middle B:Bottom

- 1) A.M. Shams El Din, Rasheed A.Arain and A.A.Hammoud(1991) A contribution to the problem of trihalomethane formation from the Arabian Gulf Water, Desalination, 8513-32.
- 2) Energy and Environmental Technology Laboratory, Electric Power Central Laboratory, "A method of measuring trihalomethane in condenser cooling water", Electric Power Central Laboratory Report, May 1982.

4. Conclusion

Literature on the measurement of oil in normal seawater is scarce but, summarizing the contents of papers extracted from our literature search, the maximum concentrations of oil in the vicinity of marine oil fields were 0.13 to 0.24 ppm.

Also, the results of oil content measurements in the seas around Japan and in the main bays were all of the order of 0.01 ppm, which is not in the range that would particularly hinder desalination processes.

According to a paper relating to trihalomethane in seawater, if the seawater is normal and natural seawater, the formation of THM in desalination plants is maintained within international standards but, it concludes, if the sea is polluted by the outflow of crude oil, etc., it is necessary to suppress the formation of THM by reducing the level of chlorination and to increase the frequency of measuring the THM content of water which is produced.

8.1.1.B. Analytical Method of Trihalomethane

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(8.1.1.B)

1. Objectives

Main objective is to study seawater soluble organic materials and their reaction with chlorine. Concerning the mechanisms for the formation of THM, it is well known that trihalomethanes are formed by the reaction of halogens such as chlorine and bromide with organic materials (precursors) which dissolve in seawater but the reaction mechanisms of the intermediate products are extremely complicated. The literature was searched on these points as an aid to considering ways of inhibiting their formation.

2. Search method

Based on the following key words, a search of the JOIS data base produced 30 items published between January 1981 and November 1993, from which paper which were closely related to the subject were selected and summarized.

- (1) Seawater x solution x organic x analysis**
- (2) Seawater x solution x organic x absorbent**
- (3) Seawater x halogenated organic compounds x (solubility + analysis + removal + formation mechanism)**

3. Results

3.1 Formation Mechanism of Organic Halogen Compounds like THM and Others

(1) Circumstances of THM Control

The Environmental Protection Agency (EPA) of the US conducted National Organics Reconnaissance Survey (NORS) in 1975. At the same time, EPA started the setting the limits of the allowable standard for organic chlorine compounds of low boiling point in tap water, the study of the formation mechanism of the compounds, and the research into it's removal method. As a result of the study, the Agency made it clear that chlorination is an important factor in the formation of halide organic compounds.

Based on the above study result, in November 1979, EPA decided to regulate the Maximum Contaminant Level (MCL) of total THM in tap water to lower than 0.10mg/l.

(8.1.1.B)

At present, the above regulation covers only tap water. The EPA suggested as the future target the values of 0.010 – 0.025mg/l, and it is expected to propose to make the treatment with granulated active carbon or the like as the matter of duty in the near future.

(2) THM Formation and Various Factors

[Definition and Varieties of THM]

In THM, 3 hydrogen of methane (CH_4), hydrocarbon of the most simple molecular structure, are substituted by halogen atoms like chlorine, iodine and bromine. Various types of THM are shown in Fig 1.

Of varieties of THM, chloroform (CHCl_3) is most frequently detected in tap water, and other THM compounds often detected are bromodichloromethane (CHBrCl_2), dibromochloromethane (CHBr_2Cl) and bromoform (CHBr_3). These four types of THM compounds are defined as total THM (TTHM: mg/l).

[Precursors]

The organic matter which functions as the precursor of THM formation is considered to be mainly humus (refer to Fig. 2), but formation of THM from tannic acid, nitrogenous organic compounds, and microorganisms which grow in rivers, lakes and marshes such as algae and chlorophyll α , is also reported. In general, aromatic compounds of hydroxyl group and amino group, and the compounds of carbonyl bonding are easy to form THM; and many organic matters other than hydrocarbon, are considered likely to function as precursors of THM. Multiplication of algae caused by the eutrophication of raw water has the possibility to increase the precursors of THM.

[Formation Reaction]

The reaction mechanism for the formation of THM from precursors and chlorine is very complicated and there are many points not clarified yet. Representative reaction examples are indicated in Fig. 3 and Fig. 4.

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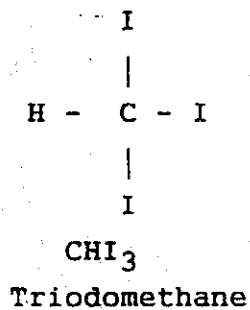
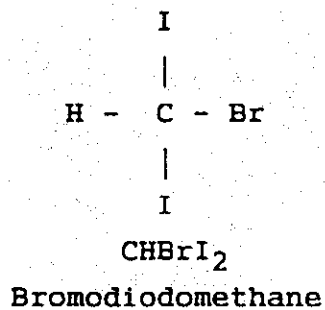
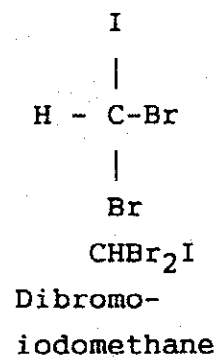
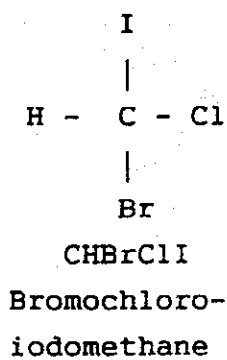
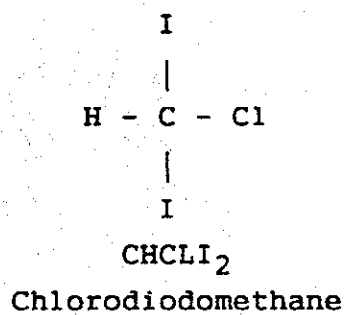
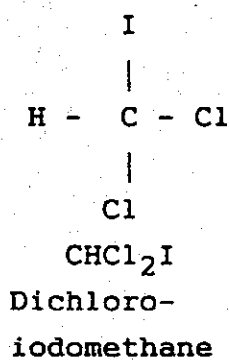
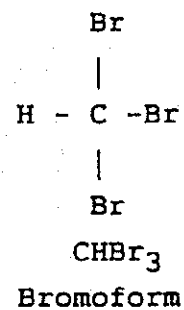
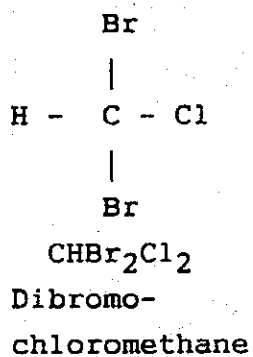
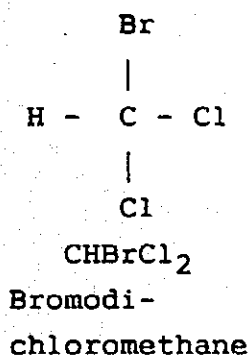
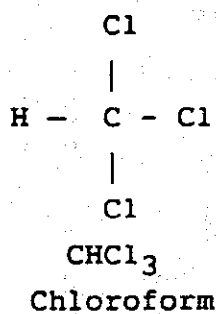
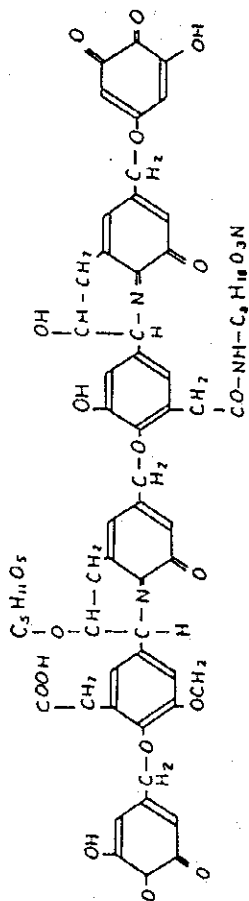
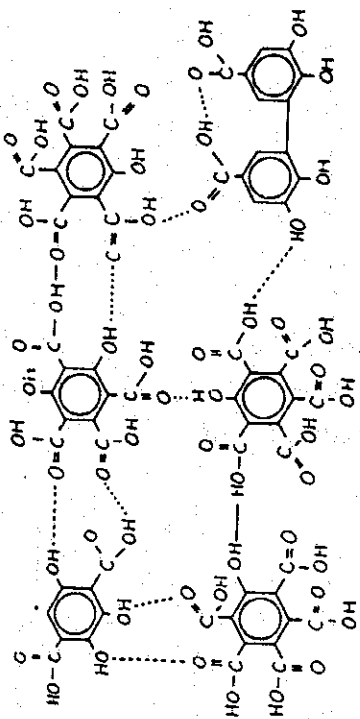


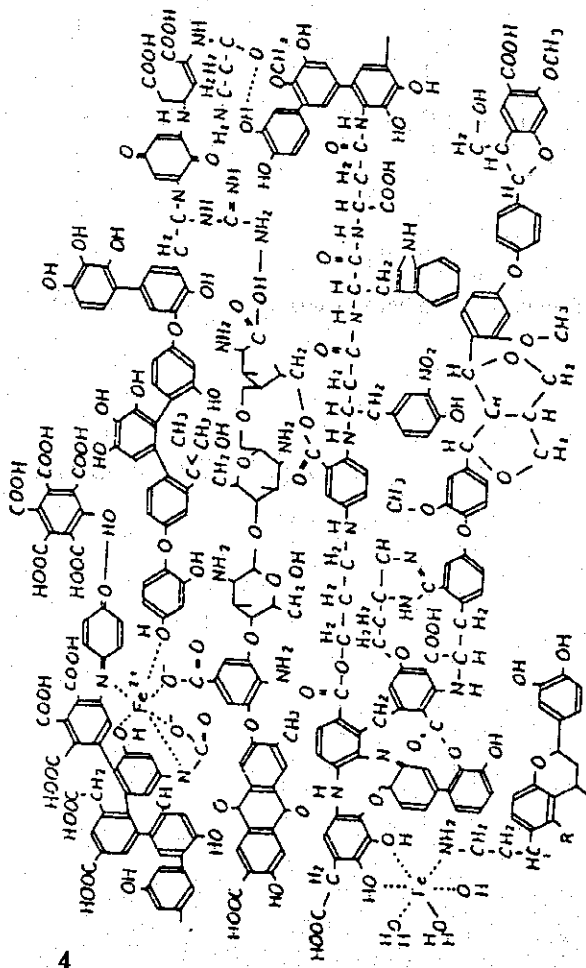
Fig. 1 Trihalomethane Compounds



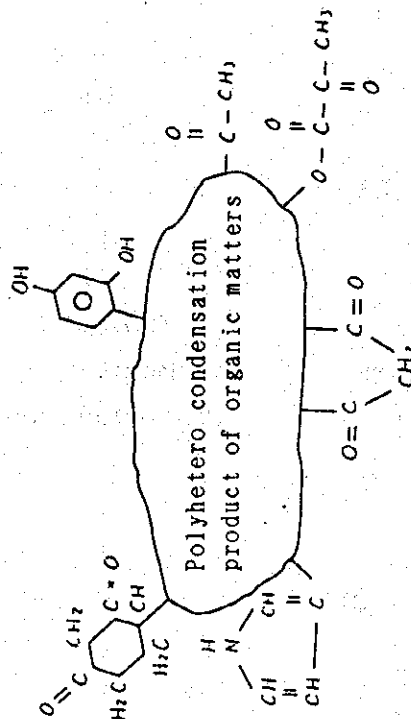
a) An estimated structural formula of humic acid



c) An estimated structural formula of fulvic acid



b) An estimated structural formula of humic acid



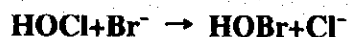
d) An overall structural formula of humic acid

Fig. 2 Estimated Structural Formulas of Humic Acid

(8.1.1.B)

When halogen ions exist in water, the reaction of $X_2+H_2O\rightarrow HOX+H^++X^-$ is induced.

As indicated in Fig. 3 and Fig. 4, HOX takes part in every reaction one after another; passing through the three processes of oxidation, chlorination and hydrolysis, it is halogenated at the end and forms THM. When hypochlorite is added to the water containing bromine ions and iodine ions, hypochlorite is easily oxidized as shown in the formula below, and forms THM containing bromine and iodine.



[Formation Conditions]

The formation amount of THM fluctuates depending on the concentration of precursors and that of chlorine. When precursors are homogeneous, the formation amount of THM and the concentration of the precursor (TOC, COD) is in a primary proportional relation (Fig. 5).

When heterogeneous precursors are contained, the interdependency of TOC and COD, and the formation amount of THM, decreases. When ammonium ions are not contained, the formation amount of THM is almost proportional to the 0.2–0.3 power of the concentration of the added chlorine (Fig. 6). When a lot of ammonium ions are contained, chlorine reacts with ammonium ions and forms chloramine and others, and only a little THM is formed.

The formation amount of THM is affected by pH (Fig. 7). Up to pH=10, when the pH is higher, that is, when the hydroxide ion concentration is higher, the hydrolysis reaction progresses more and the formation amount of THM increases. When the pH is more than 10, however, the formation amount of THM decreases. That is because, it is presumed, when pH is high, hypochlorous acid is ionized and its reaction lessens; or because the THM formed is decomposed.

The THM formation reaction speed is comparatively low, and it takes a long time for the reaction to complete (Fig. 8). Consequently, when the temperature is higher, the reaction speed is higher and the formation amount of THM after a given period of time increases. It is acknowledged that when the temperature is higher by 10°C , the formation amount of THM increases by 1.6–1.7 times.

(8.1.1.B)

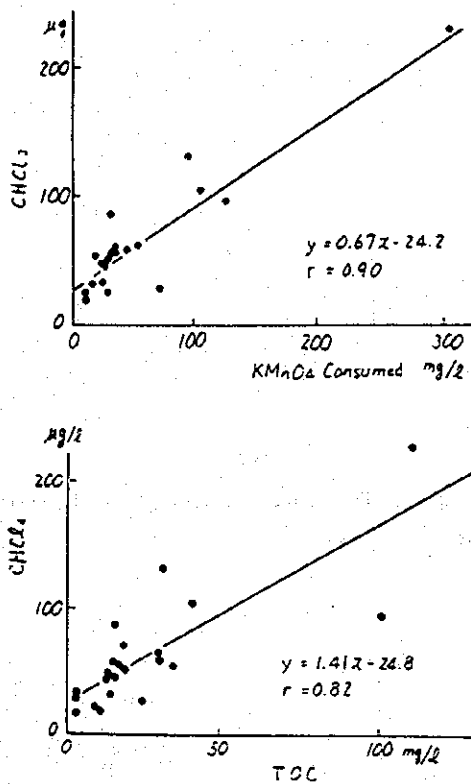


Fig. 5

Relation of the water contamination index and the formation amount of chloroform

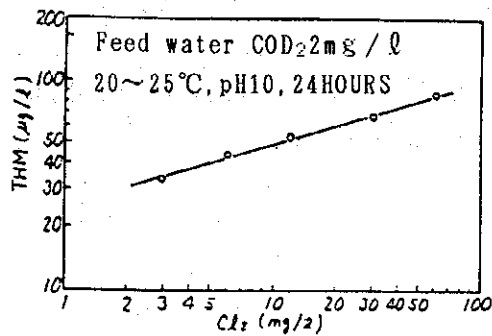


Fig. 6

Change in the formation amount of trihalomethane depending on the amount of chlorine added Humic acid

(8.1.1.B)

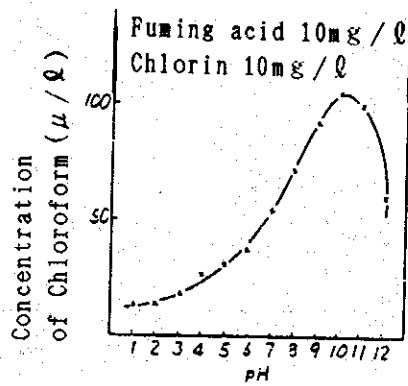


Fig. 7

Change in the formation amount of chloroform depending on pH

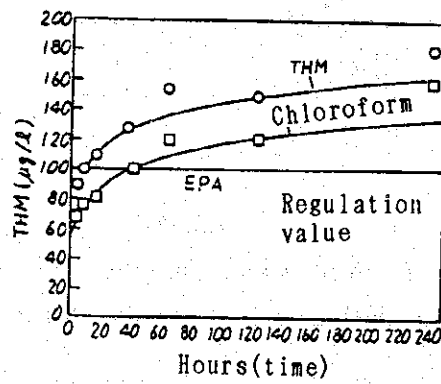


Fig. 8

Change in the formation amount of trihalomethane with time (river water)

(8.1.1.B)

To summarize the above, the relation of THM formation and various factors is as shown in Table 1 below. It is presumed that the mutual reaction of these factors determine the formation amount of THM.

Table 1 Factors to THM Formation

Factor		Formation Amount
The amount of chlorine added	a lot	a lot
The contact time with chlorine	long	a lot
The temperature of water	high	a lot
pH	high	maximum when pH=10
Water quality (COD,TOC)	bad	a lot

3.2 Analytical Method of Trihalomethane

(1) Selection of Analytical Equipment

Electron capture detector (ECD) equipped gas chromatography (GC) and GC-Mass spectrometry (GC-MS) are widely used for the analysis of halogenated organic matter such as trihalomethane (THM).

ECD-equipped GC uses a unique characteristic for showing particularly high sensitivity in respect of parent electron compounds such as those containing halogen atoms. Since one THM molecule contains three halogen atoms, ECD-equipped GC is capable of highly sensitive measurement.

As a qualitative and quantitative method for gases or liquids, GC-MS is considered to be the optimum method at present and is the main method used in the United States.

However, GC-MS equipment is expensive and difficult to popularize readily, so it is hard to see it coming into general use.

Consequently, for this proposed method, we suggest GC as analytical equipment which is easily popularized, and a method which is capable of being operated electrically.

(8.1.1.B)

(2) **Summary and Selection of Pre-treatment Methods**

There are three broad types of pre-treatment for THM measurements, shown in Table 2. These are summarized below.

Table 2 Pre-treatment methods for THM measurements

	USA	Japan
Head space method	×	○
Purge trap method	○	×
Organic solvent extraction method	○	×

[Head space method]

Widely used in Japan, the head space method uses the properties of THM as a nonpolar, low boiling point, or ganochloride which is readily vaporized from water. After collecting a specific quantity of test solution in a vial such ass that shown in Fig. 9, the vial is tightly sealed as shown in the diagram. The THM dissolved in the water is transferred to the gaseous phase by shaking and the specific quantity is introduced into the GC and detected. There is a risk of reproducibility and accuracy changing due to the conditions of the splitting operation.

(8.1.1.B)

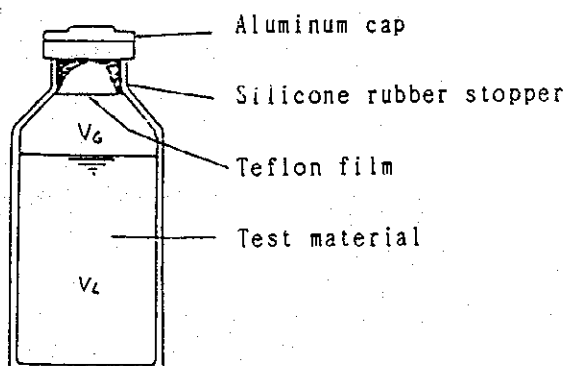


Fig. 9 Vial for Analysis

[Purge trap method]

Where the head space method is aimed at the low boiling point components, the purge trap method aims at the medium boiling point components as well as the low boiling point and is widely used in the US, together with solvent extraction methods.

In this method the test material is flushed out with diluted gas (such as nitrogen, helium, etc.) (see Figure 10) and the volatilized THM etc. is captured by an adsorbent(see Fig. 11), driven out by heat and detected separately. This method is more accurate than the head space method but measurement and pre-treatment takes more time and necessitates equipment such as flushing apparatus, concentration tube, heater, etc.

[Organic solvent extraction]

This method is aimed at measuring all organic compounds in the test material. There is a method of direct extraction by an organic solvent (see Fig. 12) and a method of adsorption in plastic in a collector followed by organic solvent extraction (see Fig. 13). This method gives abundant information but it has disadvantages such as the long time needed for analysis, due to the presence of high boiling components in the test material, and the number of GC conditions which it requires.

(8.1.1.B)

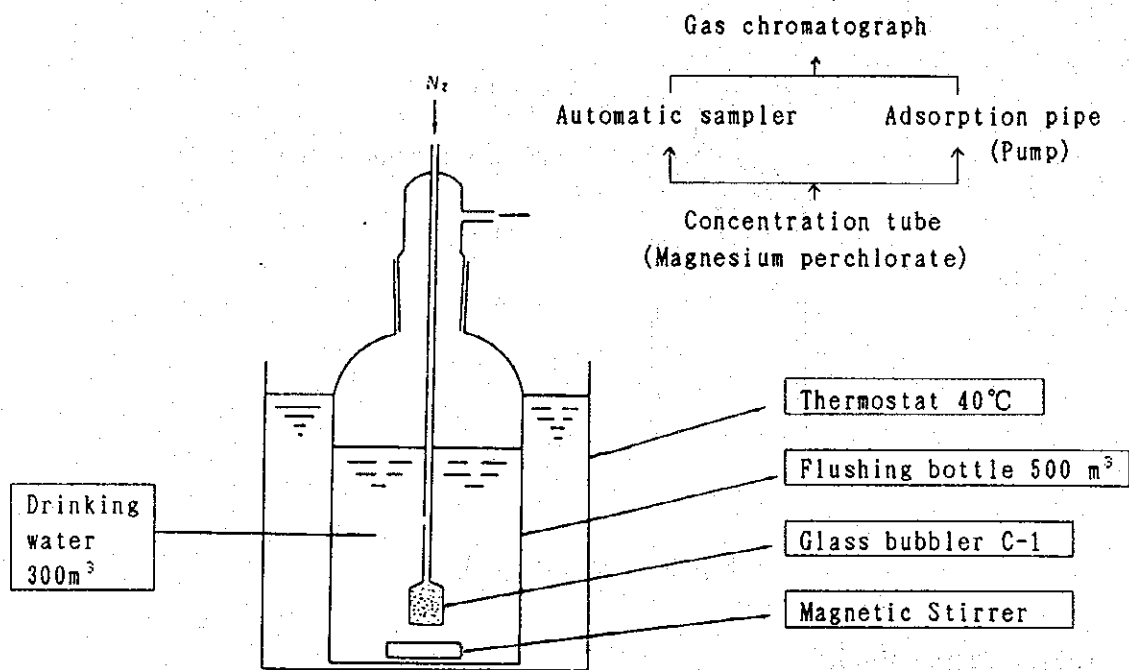


Fig. 10 Flushing Apparatus

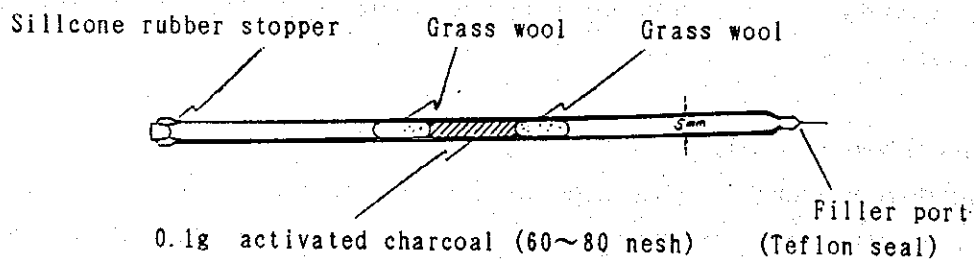


Fig. 11 Adsorption Tube

Fig. 12

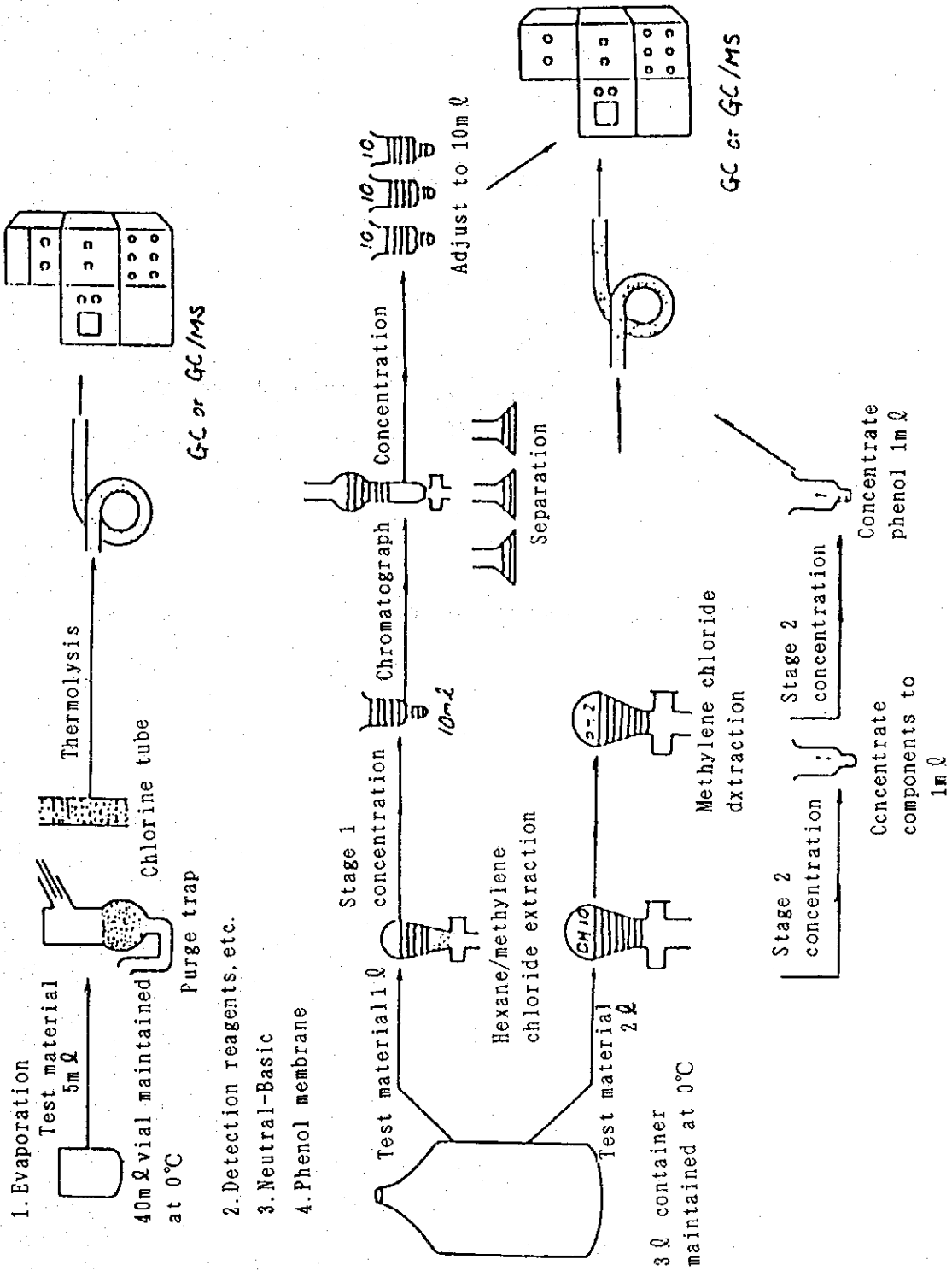


Fig. 12 Organic Solvent Extraction Method Block Diagram

(8.1.1.B)

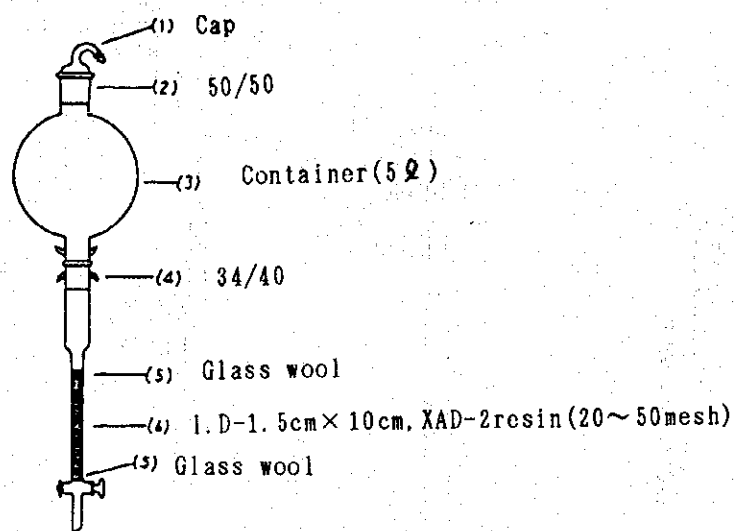


Fig. 13 Solvent Extraction Method

(8.1.1.B)

Table 3 Appraisal of THM analysis pre-treatment(table)

Pretreatment method Details	Head space method	Purge trap method	Organic solvent extraction
Pretreatment method			
Pretreatment time	⊙	○	○
Analysis time	⊙	○	△
Operating convenience	⊙	△	△
Necessary equipment	⊙	△	○
Test material handling capacity	⊙	△	△
Measuring device	⊙	○	△
Number of components detected	△	○	△
Measurement precision	⊙	○	○
Detection	△	⊙	⊙

Appraisal criteria

- (1) THM is a nonpolar, low boiling point organic compound, readily vaporized from water. Large losses and major analysis errors will occur during the operation if it is not analyzed rapidly.
- (2) In actual investigations, since several samples per hour need to be handled a method in which measurement takes as little time as possible is essential.
- (3) The method of analysis should be as simple as possible to minimize human error.

(8.1.1.B)

3.3 Studies of various conditions in measurement methods

(1) GC measurement conditions

A variety of GC conditions are presented for the measurement of THM but there are many methods which use silicone fillers.

Table 4 shows the GC measurement conditions proposed by this establishment.

Table 4 GC measurement conditions proposed by this establishment

Column	Filler	10% Silicone DC-200, Chromosorb-W, AW-DMCS,
	Length	80-100 mesh 3dmmx4m, glass column
Temperature	Column	85°C
	Intake Port	150°C
	Detector	250°C
Carrier gas	Helium 50 ml/min, 1.6 kg/cm ²	
Gas-liquid equilibrium temperature	(20 ± 0.2)°C	
Quantity of head space gas injected	0.2 ml	
Discharge gas flow	Helium 90 ml/min	

Under these conditions, as shown in Table 4, twelve types of halogenated organic matter from C1 to C2 can be measured in less than 15 minutes. However, trichlorethylene and dichloroboromomethane could not be separated.

(8.1.1.B)

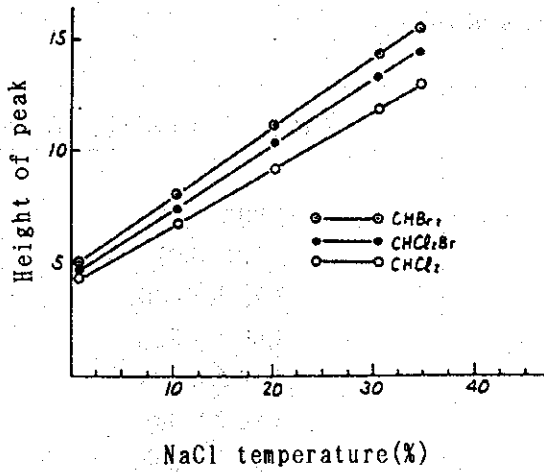


Fig. 14

Relationship between salt concentration and the amount of chloroform in the gaseous phase

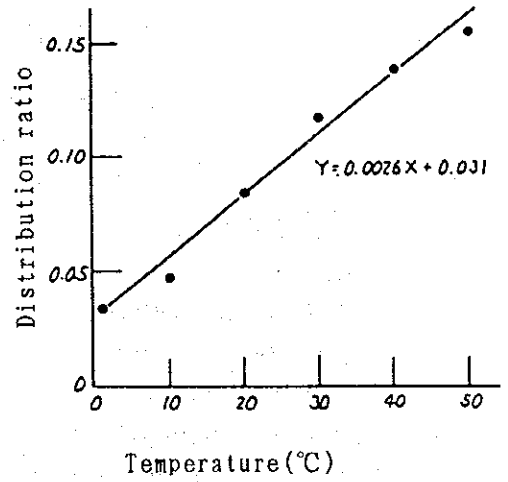


Fig. 15

Relationship between chloroform distribution ratio and temperature

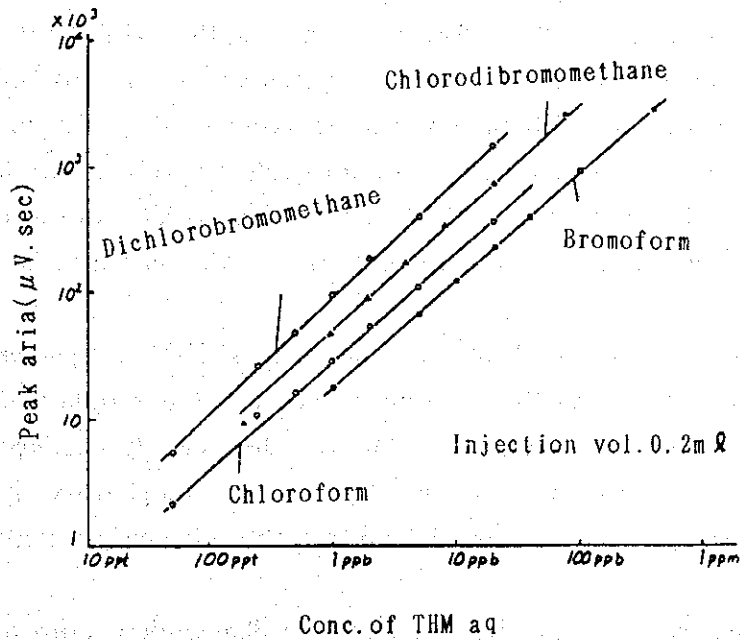


Fig. 16 Calibration Curve

(8.1.1.B)

Table 5 Retention times for each component under the GC conditions of this establishment

Component	Retention time (min)
Dichloromethane	1.90 ± 0.005
Chloroform	2.70 ± 0.011
1-1-1-trichloroethane	3.23 ± 0.006
Carbon tetrachloride	3.59 ± 0.008
Trichloroethylene	4.19 ± 0.009
Dichlorobromomethane	4.19 ± 0.009
1-1-2-trichloromethane	5.99 ± 0.093
Dibromochloromethane	6.93 ± 0.010
Tetrachloroethylene	8.31 ± 0.010
1-1-1-2-tetrachloroethane	10.00 ± 0.011
Bromoform	11.96 ± 0.007
1-1-2-2-tetrachloroethane	13.78 ± 0.005

(2) **The effect of ion intensity**

The head space GC method distributes the volatile THM between its gaseous and liquid phases and measures the THM compounds in the gaseous phase but, as shown in Figure 7.3.3-14, the distribution rate is influenced by the salt concentration (ion intensity). Since seawater is a type of inorganic electrolytic solution containing about 3.3 to 3.7% salts (salinity 3.3 to 3.7%), we used artificial seawater (JIS-K-2510-1980) to study the distribution ratios between fresh water to seawater.

The results are shown in Table 6. The various THM components in the artificial seawater are affected by the salt concentration and give values which are 25 to 5% higher than purified water, the values varying slightly between the components. Consequently, when determining the THM components in seawater, that concentration needs to be obtained from the calibration curves made with seawater.

Furthermore, as shown in Fig. 15, since the distribution ratios are affected by the temperature at the time the distribution operation is carried out, the temperature needs to be kept constant during this operation.

(8.1.1.B)

Table 6 Ratio of sensitivity of detection of THM components in fresh water and seawater (Effect of ion intensity)

Item Component	Perceived Concentration (ppb)	Peak area		Artificial seawater/ purified water
		Purified water	Artificial seawater	
Chloroform	2.68	9.05	12.1	1.34
Dichlorobromomethane	4.73	36.8	15.2	1.23
Dibromochloromethane	5.78	20.4	25.8	1.26
Bromoform	25.0	12.8	16.0	1.25

3.4 Calibration Curves and Precision

Fig. 16 shows a set of calibration curves. Table 7 shows repetitive precision. The lower limit for quantitative measurements was different for each component but in each case it was of the order of parts per trillion and we believe the reliability of the repetitive precision is quite adequate for routine tests.

3.5 Storage and Transportation of Test Materials

- (1) The effect of residual chlorine during storage when test materials with residual chlorine are transported or stored as they are, like condenser cooling water or tap water, the residual chlorine reacts with organic matter in the test materials to produce THM. As shown in Table 7.3.3-7, this trend is more noticeable at higher temperatures. This residual chlorine in the test materials also has an effect at the time of the distribution operation (Table 8).

(8.1.1.B)

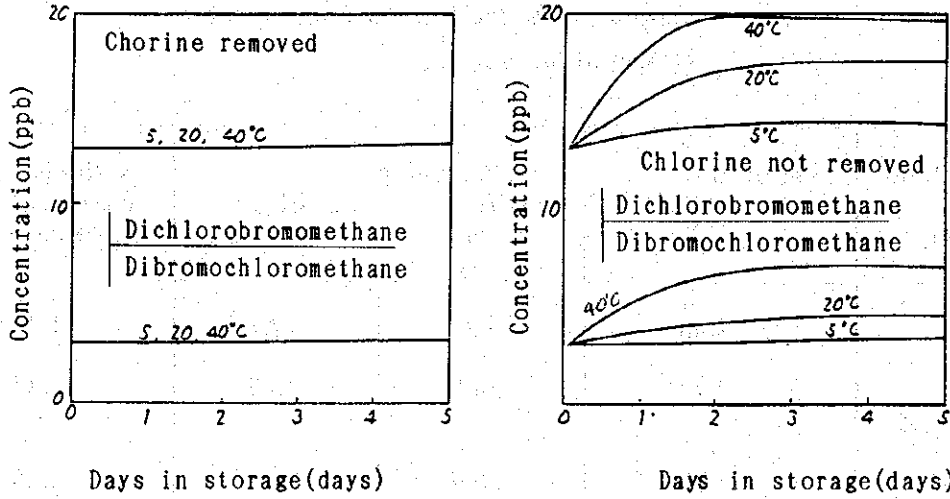


Fig. 17 Change in Quantities of Dechlorobromomethane and Dibromochloromethane in Water Occurring During Storage

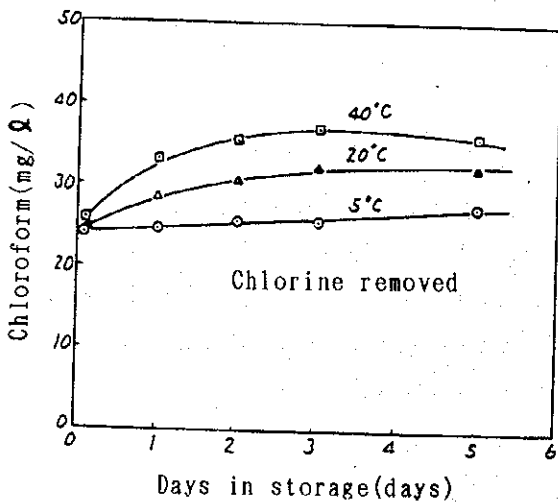


Fig. 18 Variation in temperature of chloroform due to storage hydrolysis

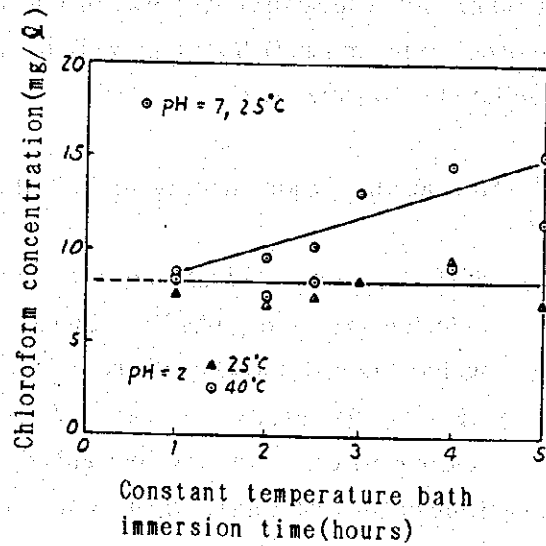


Fig. 19 Effect of reduced pH in suppressing of chloroform intermediate materials

(8.1.1.B)

Table 7. Effect of residual chlorine on storage

Temperature(°C)	24hr		96 hr	
	bsent	Present	Absent	Present
4	8.7	9.2	8.3	9.4
16	8.7	10.1	7.0	9.9
27	8.2	11.7	7.5	13.3

Note: Residual chlorine 1 ppm Test material: Chloroform

Table 8 Effect of residual chlorine at the time of the distribution operation

Residual chlorine	CHCl ₃	CHCl ₂ Br	CHClBr ₂	Unknown
Absent	0.81	1.49	0.1	-
Present	0.96	1.55	0.1	0.1

Therefore, the residual chlorine in test materials must be removed. by adding an amount of sodium thiosulphate or sodium sulphite equivalent to the concentration of residual chlorine in the test material (Fig. 7).

However, as shown in Fig. 8, chloroform is affected by storage temperature and the period of storage even after the chlorine has been removed.

(2) Chloroform and pH during storage

The effect of pH is to increase the formation of THM as the pH becomes alkaline, reaching a maximum at pH=10. Chloroform also increases during storage, even after chlorine has been removed. It is said that chloroform is formed by the hydrolysis of intermediate products of the haloform reaction.

(8.1.1.B)

Dropping the pH is a possible means of controlling the haloform reaction. The relationship between pH and chloroform formation is shown in Fig. 7.3.3-19. By reducing the pH of the test material with phosphoric acid, the increase in chloroform formation is suppressed, even at storage temperatures as high as 40°C.

Therefore, test material which have been collected must first be stripped of chlorine and the pH adjusted to 2 before they are transported or stored.

References:

Kumai, K., Yatabe, T. and Koizumi, M. (1982):

"A method of measuring trihalomethane in condenser cooling water", Laboratory Research Reports of the Energy Environment Technology Laboratory, Electric Power Central Research Institute.

3.6 The literature on the Problems of THM Formation in the Arabian Gulf

Fundamental experiments ascertain the conditions of THM formation in the distillation-process seawater desalination plant in the Arabian Gulf are being conducted by the Water and Electricity Department of the Emirate of Abu Dhabi.

Usually, the amount of THM formed in the distillation-process desalination plant of natural seawater is within the range of governmental and international standards. When the seawater is polluted with the flow-in of crude oil or other substances, however, it is necessary to reduce the formation of THM by lowering the chlorination level, and at the same time, to sample the distilled water frequently to check the formation of THM.

1) A.M. Shams El Din, Rasheed A. Arain and A.A. Hammond (1991)

A contribution to the problem of trihalomethane formation in Arabian Gulf seawater, Desalination, 8513-32

4. Conclusion

We were able to gain an understanding of analytical methods, formation mechanisms, conditions for formation, analytical precision etc. in respect of halogenated organic compounds, especially trihalomethane.

(8.1.1.B)

Quantitative lower limits differ according to the components (chloroform, bromoform, chloro-dibromonethane, dichloro-bromomethane) but in each case they are of the order of ppt and the analytical precision is extremely high.

8.1.1.C. Removal of Trihalomethane

(8.1.1.C)

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1. Objectives

To conduct a literature search in respect of tolerance to oil-bearing seawater, which could be harmful to RO membranes used in seawater desalination and a literature search concerning the removal of halogenated organic compounds such as trihalomethane to serve as a guide to the safety of future desalination technology.

2. Method of Investigation

The literature survey were centered on major technical reports.

3. Results

To separate and remove THM, an adsorption method, a membrane separation method and others have been developed. This report is a survey of the literature on the present membrane separation technology.

[Separation and Removal of THM]

Recently, there is a growing tendency to try to obtain potable water from seawater or brackish water in various countries of the world. In the desalination of seawater and brackish water near large cities, the effect of the pollution in the raw water on desalination has become far from negligible. Allowable limits of THM and bromoform have been added recently to the items of the water quality standards for drinking water, and great importance is now placed on the removal of THM.

(1) Removal of THM model substance with RO membrane

For the removal of various THM added derivatives, the performance of both the UTC-80 membrane of the fully aromatic polyamide composite membrane and the SC-8000 membrane of the cellulose acetate (CA) membrane, are indicated in Table 1.

In the permeate of the UTC-80 membrane, almost all THM substances detected were less than 10ppb each. For example, the detected amount of chloroform was less than 9.5ppb and bromoform was less than 1ppb, the removal rate being more than 95% and 99.3% respectively. On the other hand, the concentration of each THM substance in the permeate of the SC-8000 membrane was almost the same as that of the feed water. From this experiment, it is obvious that the THM removing rate of the cross-linked

(8.1.1.C)

fully aromatic polyamide composite membrane is much higher than that of the CA membrane.

Table 1 Trihalomethane Separating Performance of the UTC-80 Membrane and the Cellulose Acetate Membrane

Trihalomethan	UTC-80		Cellulose Acetate		
	Feed liquid (ppb)	Permeated liquid (ppb)	Removal rate (%)	Permeated liquid (ppb)	Removal rate (%)
Chloroform	190	9.5	95.0	190	0
Chlorodibromomethane	195	1.4	99.3	150	23
Bromodichloromethane	175	3.7	96.0	150	14
Bromoform	145	< 1	>99.3	120	17
Dichloroacetate	130	<10	>92.0	-	-
Trichloroacetate	190	3	98.0	-	-
Chloroacetonitrile	170	69	59.0	-	-
Chloralhydrate	190	6.4	97.0	-	-
Trichloroethylene	150	< 1	>99.3	88	41
Trichloroethane	130	< 1	>99.2	95	27
Tetrachloroethylene	135	<0.5	>99.6	60	56
Membrane performance	99.67%-0.55m ³ /m ² day 97/1%-0.49m ³ /m ² day				

Measuring conditions : 3.5% NaCl, 25°C, pH6.5, 5.5Mpa

Measurement was carried out after adding trihalomethane substances in the feed liquid.

*Reference: D. Cormack: Response to oil and chemical marine pollution, Applied Science Publishers Ltd.

(2) Affinity to trihalomethane and membrane

The desalinating rate of the UTC-80 membrane is also higher than that of the SC-8000 membrane, but the difference in the THM removing rate is far greater. It is estimated that the cause for this great difference is that CA's affinity for THM is stronger than that of polyamide; THM easily adheres to the CA membrane. From the membrane material and THM solubility parameters, it is known that CA is more hydrophobic than polyamide and that it has a high affinity for THM. The separating performance of a membrane depends on the affinity between the membrane material

(8.1.1.C)

and the object of separation, on the pore diameter, and on operation conditions (pressure). As the UTC-80 membrane has a low affinity for THM, it is hard for THM to adhere to the membrane surface or pores, and consequently it is hard for THM to permeate through the membrane. On the other hand, as CA has a higher affinity for THM than for water, THM easily adheres to the CA membrane surface or pores, and permeates through the membrane.

In this way, if the affinity between a membrane and a solute is high, it is considered likely that the solute, rather than water, will be selectively taken into the membrane pores and concentrated in the permeated liquid.

(3) Trihalomethane removing performance of a commercial plant

In a real plant, THM was added to the seawater, and then the THM removing performance was measured (Fig. 1). The SU-800 membrane element indicated a high THM removal rate of 90%. The cross-linked fully aromatic polyamide composite reverse osmosis membrane is considered more suitable than the CA membrane for potable water production plants which aim at removing THM.

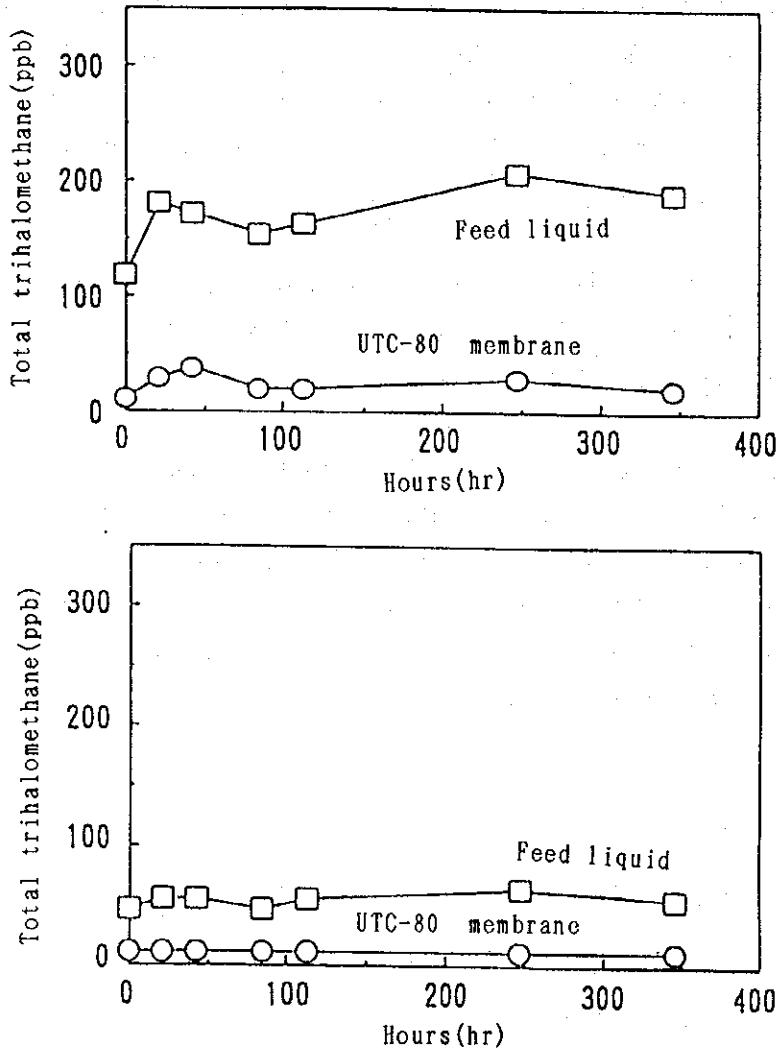
4. Conclusion

A literature survey was conducted with respect to the ratio of trihalomethane removed by RO membranes. Depending on the type of RO membrane, and its affinity to THM removal ratios as high as 99.6% were observed. It will now be necessary to verify the periods of operation over which such high removal ratios can be maintained.

1) Yu Kurihara, Spiral Membrane, Water Re-use Promotion Center Japan.

"Gists of Lectures Given in the Study Course of Advanced Water Production Technology" (Nov. 29-30, 1993.)

(8.1.1.C)



Measuring equipment : Ehime Test Plant
Measuring conditions : sea water, 25°C, pH6.5, 5.5MPa
Measurement was carried out after adding trihalomethane substances in the feed liquid (sea water).

Fig. 1 Membrane's performance of separating the trihalomethane added in the sea water

*Reference: M. Kurihara: "Spiral RO membrane," proceeding of Seawater Desalination Seminar, Sponsored by WRPC, Japan Nov. 29~30, 1993

**8.1.2 Preparative Experiment
with Laboratory Scale Equipment**

8.1.2.A. Analytical Methods for Low Concentrated Oil

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(8.1.2.A)

1. Studies of Various Methods

The conventional, standard methods of oil analysis are the n-hexane (mass) method and the carbon tetrachloride extraction (infrared) method. Detection limits are of the order of parts per million.

When crude oil flows into sea water, the dispersed oil content in sea water is extremely low. With these conventional methods of oil analysis, the measurement and assessment of the capacity for removing such low oil concentrations is considered to be extremely difficult and the ability to measure these lower oil concentrations is needed.

The test material to be handled by this project has the following characteristics:

- Low oil content
- Many test samples
- Due to experimentation, some samples to be analysed are small

Therefore, the method of analysis to be used here must be quick, simple to operate and have low limits of detection.

Here, we study methods of oil analysis which satisfy these conditions.

1.1 The n-Hexane Method (Mass Method)

(1) Principle

Used as a standard method of analysing oil content.

Mainly suited to the quantitative analysis of non-volatile mineral oils and animal and vegetable oils and fats. The oil content is extracted with n-hexane and the residue (the hexane extractant) is determined after evaporating the hexane at 80°C. The limit of detection is 5 ppm in one liter of sample used. If the oil concentration is low (but greater than 0.5 ppm), the oil is measured after precipitation and concentration using ferric chloride (1.1).

With this method, low boiling point components are volatilized during the evaporation operation.

(8.1.2.A)

(2) Results of Study

This method not only has low detection limits but it is clearly unsuitable for this project because of the time needed to evaporate the sample.

1.2 The Carbon Tetrachloride Extraction Method (Infrared Method)

(1) Principle

Used as an official method of analysing oil content.

During extraction with hydrochloric acid, hydrogen chloride derivatives, animal and vegetable oils and fats, fatty acids, etc. present in the sample are extracted. Infrared absorption in the carbon tetrachloride solution is measured and expressed in relation to a standard mixture of iso-octane, octane and benzene (OCB standard). The limit of detection is 0.2 mg OCB.^{1,2} Since this method involves only extraction, low boiling point components can also be analysed.

(2) Results of Study

This method uses carbon tetrachloride as the extraction medium but it is considered unsuitable for this project due to the difficulty of SWCC obtaining good quality carbon tetrachloride and the increased bulk of sample material required in order to increase the limits of detection.

1.3 Simple Analysis Method

(1) Principle

The sample material is placed in a test cell inside the equipment together with carbon tetrachloride, agitated and extracted by a motor inside the equipment. The extracted oil content is measured by an infrared analyser inside the apparatus. The principle is the same as that for the carbon tetrachloride extraction method (infrared method).

This is the method which has been used up to now in the SWCC/JICA Project for the analysis of the oil content of sea water.

(2) Results of Study

The operation is almost entirely automatic and extremely fast, requiring only one or two minutes per sample. Nevertheless, fresh carbon tetrachloride is not available at SWCC and, as it deteriorates, the high background makes calibration impossible.

(8.1.2.A)

The maximum amount of sample is only 15 ml and the low limit of detection makes this method unsuitable for oil content analysis for this project.

1.4 TOC Method

(1) Principle

The sample, together with air from which carbon dioxide has been removed, is passed through a tube filled with an oxidation catalyst for total carbon measurement and a tube filled with an acidic catalyst for inorganic carbon measurement. The inorganic carbon content is subtracted from the total carbon content measured by an infrared analyser.

Range of measurement: 4 ppb to 4000 ppm at Cl⁻ content of 3% or less (with a Shimadzu TOC-5000).¹³

(2) Results of Study

1) Correlation with carbon tetrachloride extraction (infrared method)

We investigated the correlation of this method with the carbon tetrachloride extraction (infrared method) which is used for official oil content measurements.

Apparatus and reagents

Ultrasonic cleaner (Branson B 5200; 47 kHz, 120 W)

Erlenmeyer flask (one liter)

Pure water

Fuel oil A

TOC analyser (Shimadzu TOC-5000)

Beaker

Pipette

Procedure

A dispersion of oil in water was prepared using the following procedure and we made a correlation of the oil content measured by the TOC method and by the IR method. Because of the high background due to inorganic carbon in the sea water used for measurements of the oil content in sea water by this method, it was difficult to make

(8.1.2.A)

accurate measurements of minute concentrations of oil in particular so, in this case, we have used pure water instead of sea water to investigate the correlation.

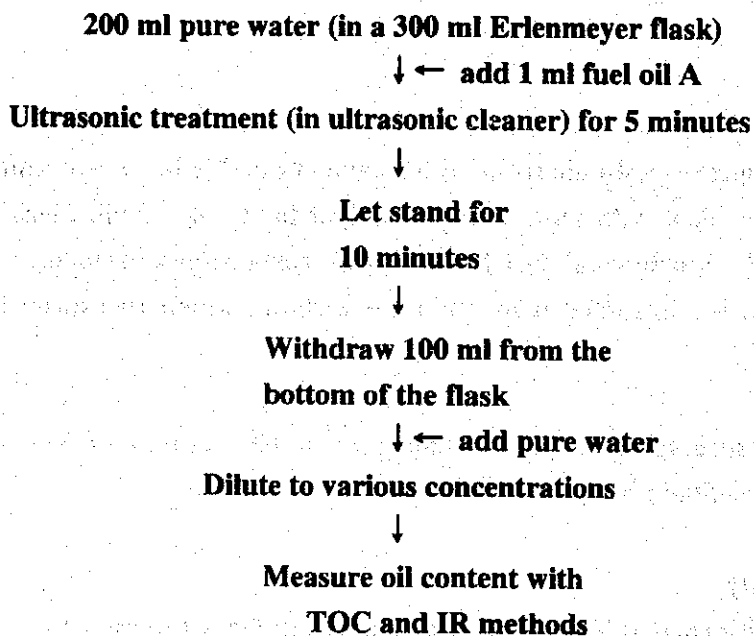


Fig. 1 Measurement of oil content in sea water using TOC and IR methods

(3) Results and Discussion

1) Correlation with carbon tetrachloride extraction (IR method)

Table 1 shows the results of comparing TOC and IR methods

Table 1 Comparison of TOC and IR methods using artificial oil-contaminated sea water

Sample	Oil concentration [ppm]		(3)/(1)
	TOC Method	IR Method	
A	2.9	5.3	1.8
B	9.0	16.4	1.8

(8.1.2.A)

Table 1 shows the results of measuring the oil content by both TOC and IR methods. The oil content values given by the TOC method are smaller than those for the IR method but the ratio is constant at 1.8. In the TOC method, the sample is measured as a number of carbon atoms by high temperature combustion and conversion into CO₂. The IR method is a completely different principle of measurement based on the absorption due to the energy of bonding between the carbon atoms.

The fact that the values measured by TOC and IR do not agree is thought to be due to the difference in the principles of measurement and calibration differences.

2) Range of Measurement

Sample concentrations from 100 ppb can be measured. (This is the smallest graduation on the SWCC TOC meter)

This method has many advantages, including fact that the amount of sample required is several tens of microliters, it is simple to operate and the measurement time is only five to ten minutes. However, the high background due to inorganic carbon in the sea water and there is comparatively large variation in measurements because the sample needs to be injected manually in the SWCC apparatus.

Therefore, its application to the measurement of extremely low oil contents is difficult.

1.5 Gas Chromatography

(1) Principle

The sample is extracted with an organic solvent such as carbon tetrachloride and measurements are taken from the area or peak heights on a gas chromatogram.

(2) Results of Study

Apparatus and reagents

Ultrasonic cleaner (Branson B 5200; 47 kHz, 120 W)

Separating funnel (100 ml)

Gas chromatography equipment

Fuel oil A

(8.1.2.A)

Carbon tetrachloride (Wako, special grade)

Procedure

1) Standard sample preparation

- Place 0.012 g of fuel oil A in a 100 ml measuring flask and make up to standard volume with carbon tetrachloride (120 ppm).
- Make samples between 1 and 100 ppm by diluting the above material with carbon tetrachloride.

2) Adjustment of oil dispersion in sea water

- Add 2.5 ml of fuel oil A to 500 ml of sea water in a one liter Erlenmeyer flask and treat in the ultrasonic cleaner for 10 minutes.
- After standing for 10 minutes, siphon off 200 ml from the lower part of the flask.
- Dilute the above material in varying degrees with sea water.

3) Analysis of standard sample

- Place the samples prepared in the above step into special vials and use them in the auto-sampler. (The samples will be treated under prescribed conditions by the gas chromatograph.)

4) Analysis of oil contaminated sea water

- Add 2 ml of carbon tetrachloride to 20 ml of the diluted sample prepared above and shake three times for 20 seconds in the separating funnel to extract the oil content from the sample.

(This operation concentrates the sample by a factor of ten.)

- Place the oil contents which have been extracted into the carbon tetrachloride phase into special vials and use them in the auto-sampler.

(The samples will be treated under prescribed conditions by the gas chromatogram.)

GC Measurement Conditions

Analytical equipment : Shimadzu GC-17A

Recorder : Shimadzu CR-6A

Column : DB-1 (0.25 mm x 25 m, non-polar)

(8.1.2.A)

Sample injection quantity : 0.5 μ l

Split ratio : 1:10

Column opening temperature : 280°C

Detector temperature : 310°C

Column heating conditions : 50°C, 5 min.

10°C/min. (50 to 280°C)

280°C, 10 min.

(3) Results and Discussion

1) Results of study with standard samples

Chromatograms

- With the 120 ppm A type oil sample in the column, the peaks were clearly separated but with extremely low concentration samples, it was difficult to distinguish the peaks derived from the sample from the peaks caused by noise (Fig. 2).

Measurements based on detectable peak areas

- Detectable peaks vary according to the recorder detection sensitivity and sample (fuel oil A) concentration. Also, since peaks due to components other than n-paraffin contained in the sample can not be distinguished from the base line, it is not possible to make a quantitative analysis from the peak areas of all components.
- It is possible to make a working curve from the area of the n-paraffin peaks in the components.

For example, by drawing a working curve from the sum of the areas of three of the large n-paraffin peaks with retention times of 24.9 min., 26.2 min. and 27.4 min., we confirmed a concentration of 5 ppm (Figs. 3 and 4).

However, as oil concentration falls, all the peaks used for determination can not be detected and concentration is lost.

(8.1.2.A)

2) Results of study with oil dispersed in sea water

Component distribution compared with standard samples

- Chromatograms of samples of fuel oil A dispersed in sea water and extracted with carbon tetrachloride are not greatly different from those of the standard samples (Fig. 5).

Consequently, it can be said that the working curves prepared for standard samples can also be used for the determination of oil dispersed in sea water.

Comparison with TOC Method (Table 2)

- Oil content measurements made with the TOC method and gas chromatography for samples of oil-sea water dispersion diluted to varying degrees with sea water showed major differences. "Undiluted" samples in particular varied by as much as five times.

This is thought to be due to the TOC method measuring only the oil content which is dispersed in the sample while the gas chromatography method measures this as well as the oil which floats up to the surface in the container and that clinging to the walls of the container, which is extracted by the carbon tetrachloride, producing results which are higher than those of the TOC method, especially in the case of medium to high concentrations. Furthermore, the reason that there is no great difference between the TOC and gas chromatography methods in the low concentration regime is thought to be that with low concentration samples, the amount of oil floating to the surface and clinging to the sides of the container is small.

From the above, this method can be summed up as follows:

- Detectable peaks vary according to recorder sensitivity and sample (fuel oil A) concentration making quantitative analysis using all component peaks impossible.
- It is possible to derive working curves from the n-paraffin peaks of some components. In this case, accurate determinations can be made to 5 ppm.
- For samples with very low concentrations, it is difficult to distinguish between noise and peaks derived from the sample.

(8.1.2.A)

- **There is no great difference between the chromatograms of samples of fuel oil A dispersed in sea water and extracted with carbon tetrachloride and those of the standard samples.**
- **There is hardly any correlation between TOC and gas chromatography methods in respect of samples with medium to high concentrations.**

This method has the fatal disadvantage of not being capable of measuring large numbers of samples because of the length of time required to make measurements.

(8.1.2.A)

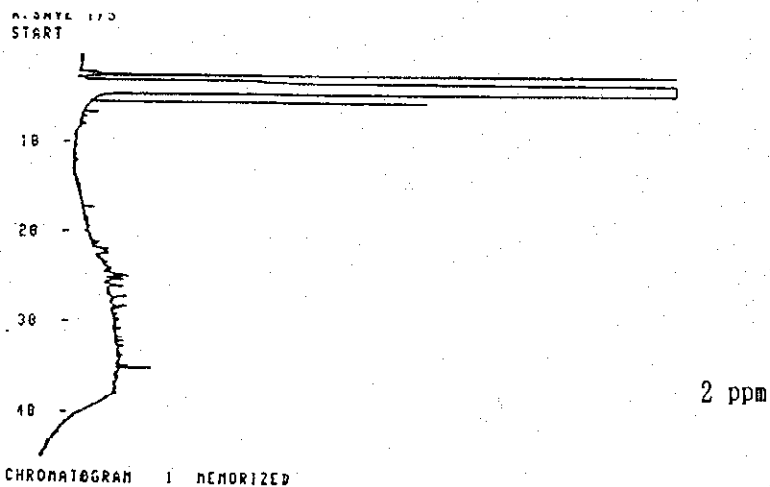
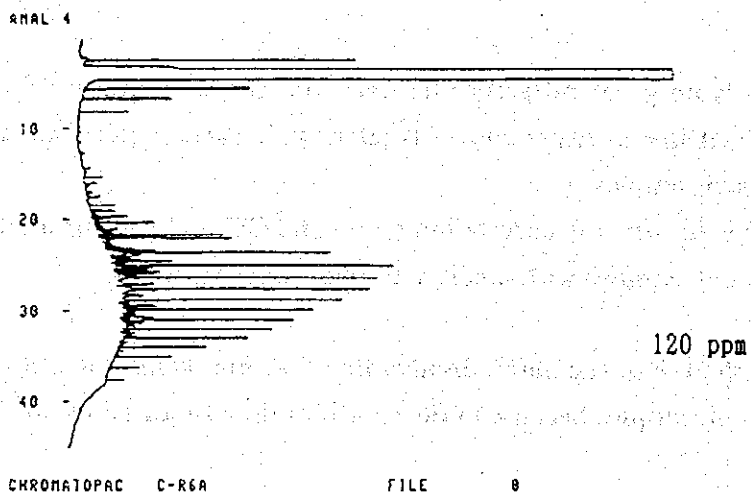


Fig. 2 Chromatograph for Fuel Oil Type A

(8.1.2.A)

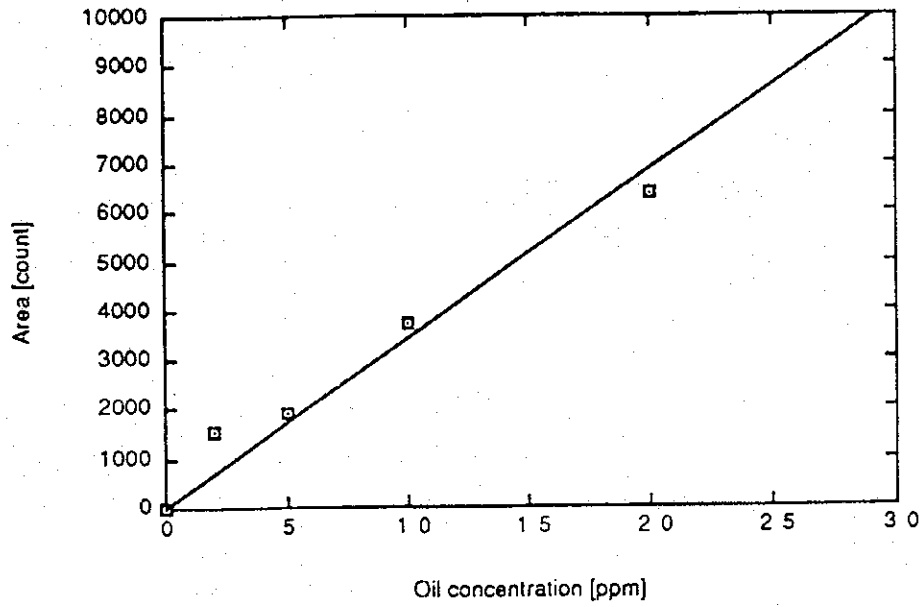


Fig. 3 GC Calibration Curve for Fuel Oil Type A (1)

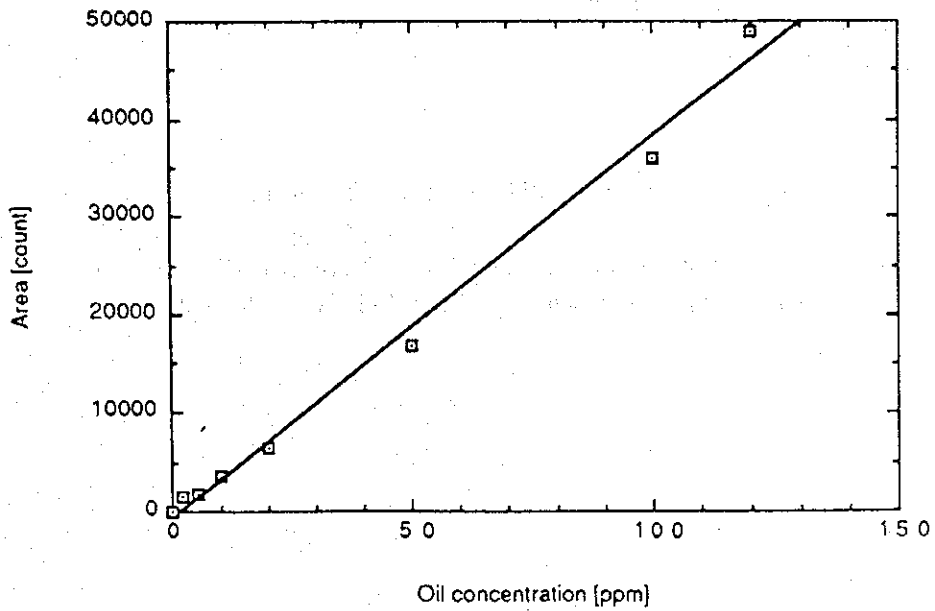
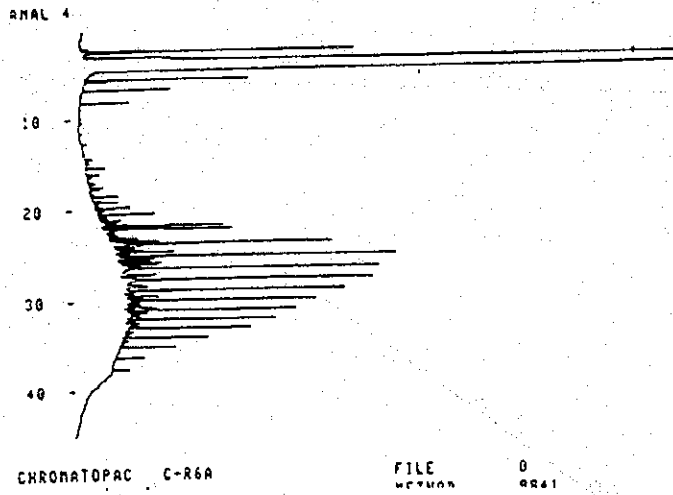


Fig. 4 GC Calibration Curve for Fuel Oil Type A (2)

(8.1.2.A)



Standard Test Material (Fuel Oil Type A)

MIN. AREA(9)=1600000
ANAL 1

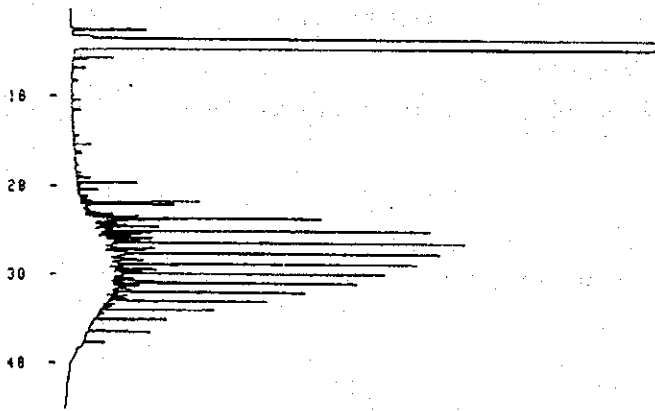


Fig. 5 Comparison of Chromatograms for Standard Test Material (Fuel Oil A) and Seawater Containing Dispersed Oil (Fuel Oil Type A/Seawater)

(8.1.2.A)

Table 2 Results of Measurement of Oil Content by TOC Method and GC Method

Test Material	Oil Concentration [ppm]		GC/TOC
	TOC Method *1	GC Method **2	
1	12.8	66	5.2
2	5.8	9.1	1.6
3	2.2	1.6	0.7
4	1.0	0.4	0.4
5	0.5	0.4	0.8
6	0.4	Nil	-

***1.2.1 : Value after subtracting the TOC zero adjustment for seawater (3.1 ppm)**

***1.2.2 : Value calculated from calibration curve in Figs. 3 and 4 adjusted for concentration of test material (10 x) during carbon tetrachloride extraction operation**

1.6 Fluorophotometry

(1) Principle

When light shines on solutions containing fluorescent materials, molecular activation is generated by the excitation of ultraviolet rays, etc. This is a method of measuring the fluorescence generated when it reverts to its basic state. The direct relationship between the strength of the fluorescence and the concentration of fluorescent materials enables quantitative analyses to be made of their concentration.

Oils, including fuel oil, are hydrocarbons which fluorescence due to the presence of aromatic rings but not the aliphatic components of the oil.

With this method, after extracting the test material with an organic solvent such as iso-octane, the fluorescence generated by the aromatic rings contained in the test material is measured and quantified on the basis of working curves derived from previously prepared sample material.

(8.1.2.A)

(2) Experimental method

(2)-1 Determining optimum fluorescence and excitation wavelengths

Apparatus and Reagents

Fluorophotometer (Nihon Bunko FP-770)

Fuel oil A standard solution (1 ppm, dissolved in iso-octane)

Fluorescence measuring cell

Procedure

Optimum fluorescence and excitation wavelengths were determined using the procedure shown in Fig. 6.

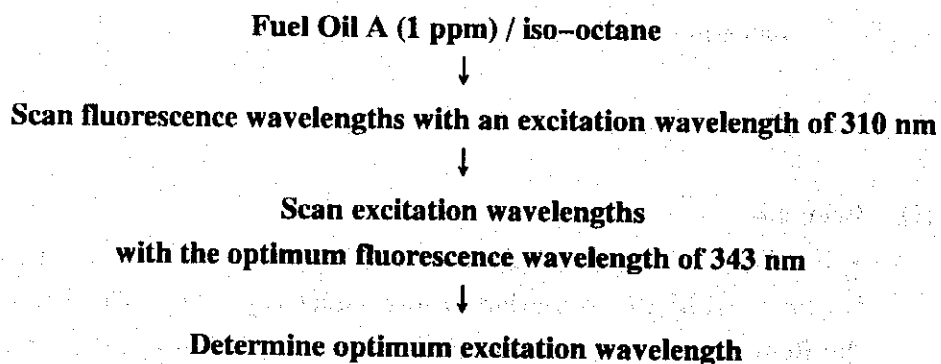


Fig. 6 Method of determining optimum fluorescence and excitation wavelengths

Measurement conditions

Slit width : excitation 10 nm, fluorescence 10 nm

(2)-2 Preparation of working curves

Apparatus and reagents

Fluorophotometer (Nihon Bunko FP-770)

Fuel oil A

100 ml beaker

(8.1.2.A)

Iso-octane (Kanto Chemicals for fluoroscopic analysis)

Measuring flask (50 and 100 ml)

Hall pipettes (various types)

Glass pipettes (various types)

Rubber tubing

Procedure

1) Preparation of standard test material

Standard test materials were prepared in accordance with the procedures shown in Fig. 7

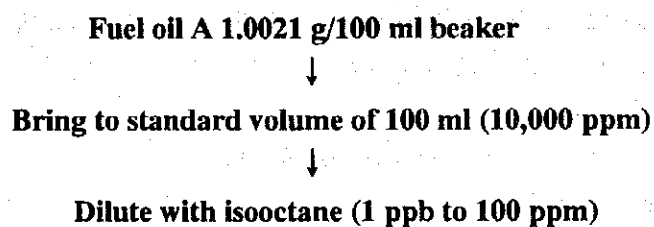


Fig. 7 Preparation of standard test materials

2) Analysis of standard test materials

Fluorescence was measured in accordance with the procedures shown in Fig. 8 and working curves were prepared.

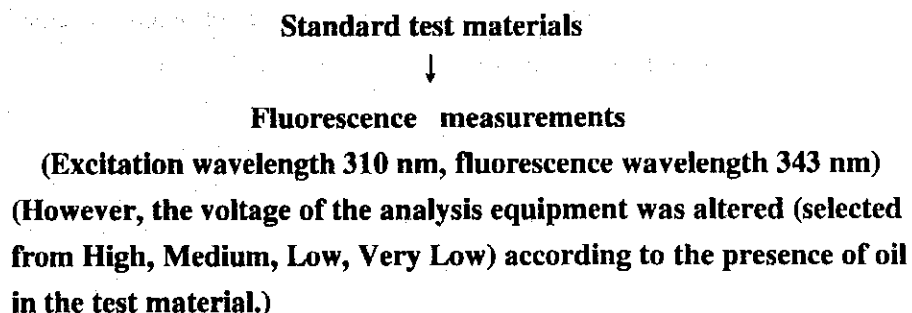


Fig. 8 Analysis of standard test materials

(8.1.2.A)

Measurement conditions

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

(2)-3 Study of methods of extraction or actual samples

Apparatus and reagents

Fluorophotometer (Nihon Bunko FP-770)
Separating funnel shaker (Iwaki KM-Shaker V-SN)
Supersonic cleaner (Branson B 5200; 47 kHz, 120 W)
Separating funnel (100 ml)
Fuel oil A
Isooctane (for fluoroscopic analysis)
Glass funnel
Filter paper (5A)
Sea water
Anhydrous sodium sulfate (special grade)
Measuring flask (25 ml)

Experimental Procedure

Firstly, sea water containing dispersed oil was prepared using the procedures shown in Figs. 9 and 10.

(8.1.2.A)

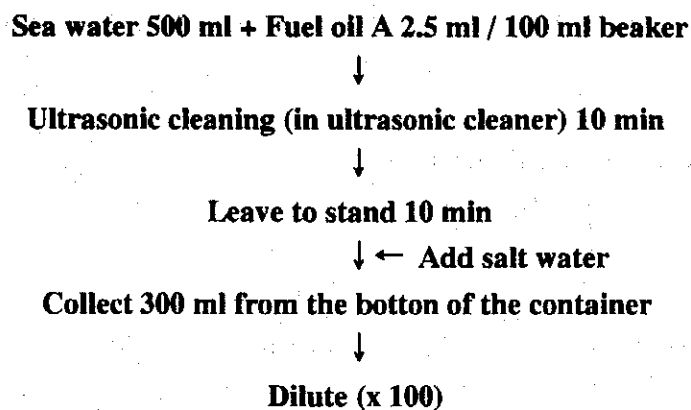


Fig. 9 Method of preparation of sea water containing dispersed oil for use in studying extraction conditions (1)

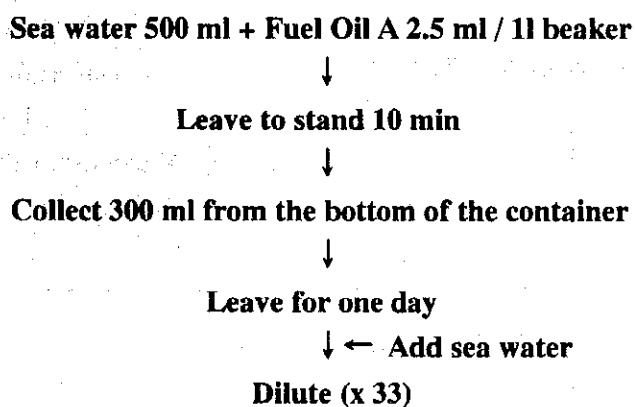


Fig. 10 Method of preparation of sea water containing dispersed oil for use in studying extraction conditions (2)

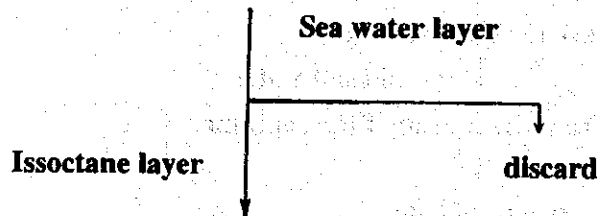
1) Study the amount of isooctane used in extraction

The amount of isooctane used in extraction was studied using the procedure shown in Fig. 11. The sea water containing dispersed oil was prepared according to Fig. 9, "Method of preparation of sea water containing dispersed oil for use in studying extraction conditions (1)".

(8.1.2.A)

Sea water containing dispersed oil 50 ml + isoctane 5 or 10 or 20 ml/100 ml separating funnel

Shake (in shaking machine) 5 min



Filter through 5A filter paper
(place a suitable quantity of anhydrous sodium sulphate on the filter paper to dehydrate the filtrate)

Collect in 25 volumetric flask

Make up to 25 ml with isoctane

Measure fluorescent intensity
(Ex. 310 nm, Em. 343 nm)

Previously used separating funnel

Isooctane 10 ml

Shake lightly

(to clean the inner wall of the separating funnel)

Wash the previously used filter paper

Fig. 11 Method of studying the quantity of isoctane used in extraction

Measurement conditions

Slit width : excitation 10 nm, fluorescence 10 nm

Excitation wavelength : 310 nm

Fluorescence wavelength : 343 nm

(8.1.2.A)

2) Repetitive extraction study

The amount of isooctane used in extraction was studied using the procedure shown in Fig 12. The sea water containing dispersed oil was prepared according to Fig. 9, "Method of preparation of sea water containing dispersed oil for use in studying extraction conditions (1)".

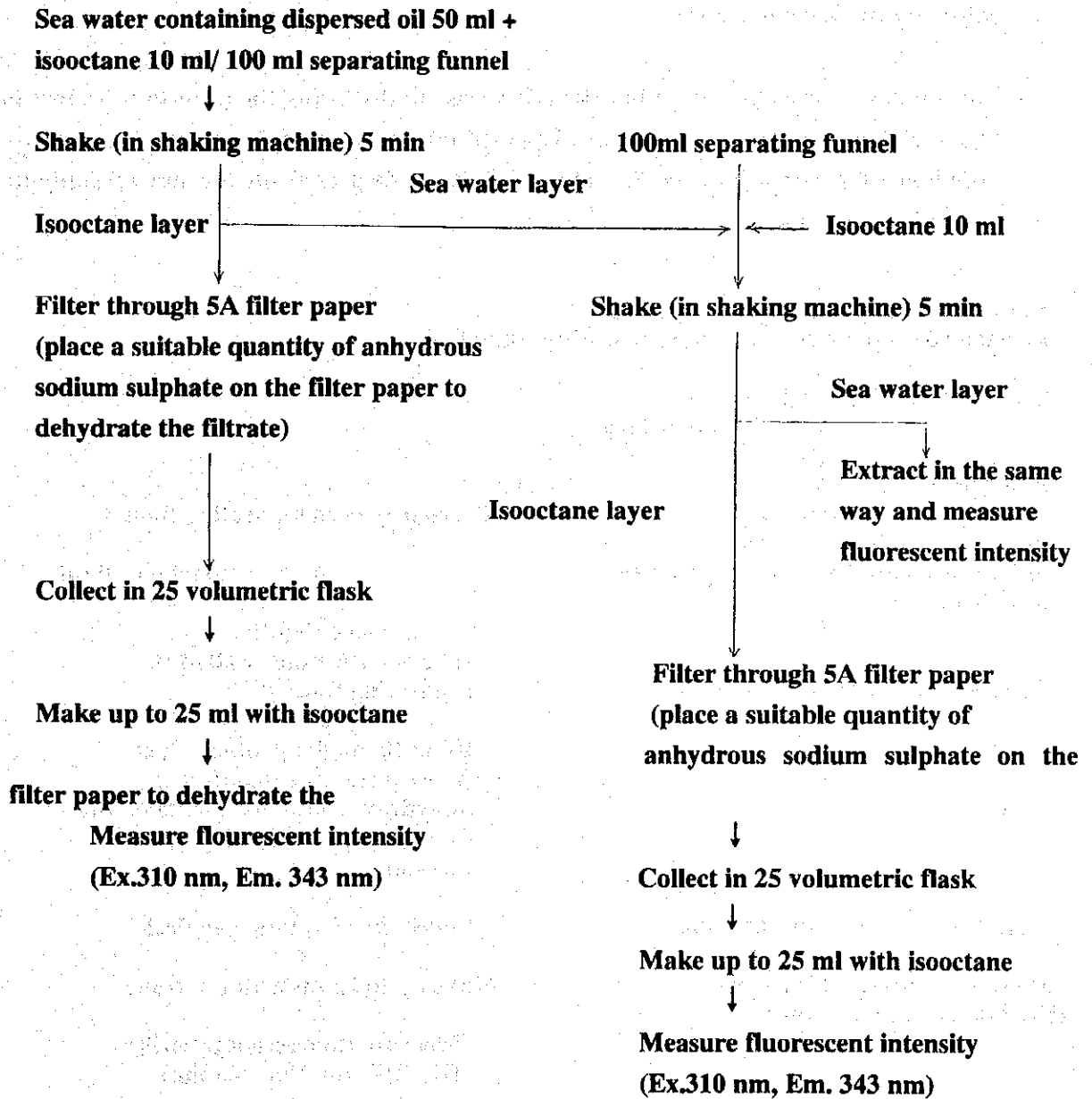


Fig. 12 Repetitive extraction study method

(8.1.2.A)

Measurement conditions

Slit width : excitation 10 nm, fluorescence 10 nm

Excitation wavelength : 310 nm

Fluorescence wavelength: 343 nm

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

The amount of isooctane used in extraction was studied using the procedure shown in Fig. 13. The sea water containing dispersed oil was prepared according to Fig. 10, "Method of preparation of sea water containing dispersed oil for use in studying extraction conditions (1)".

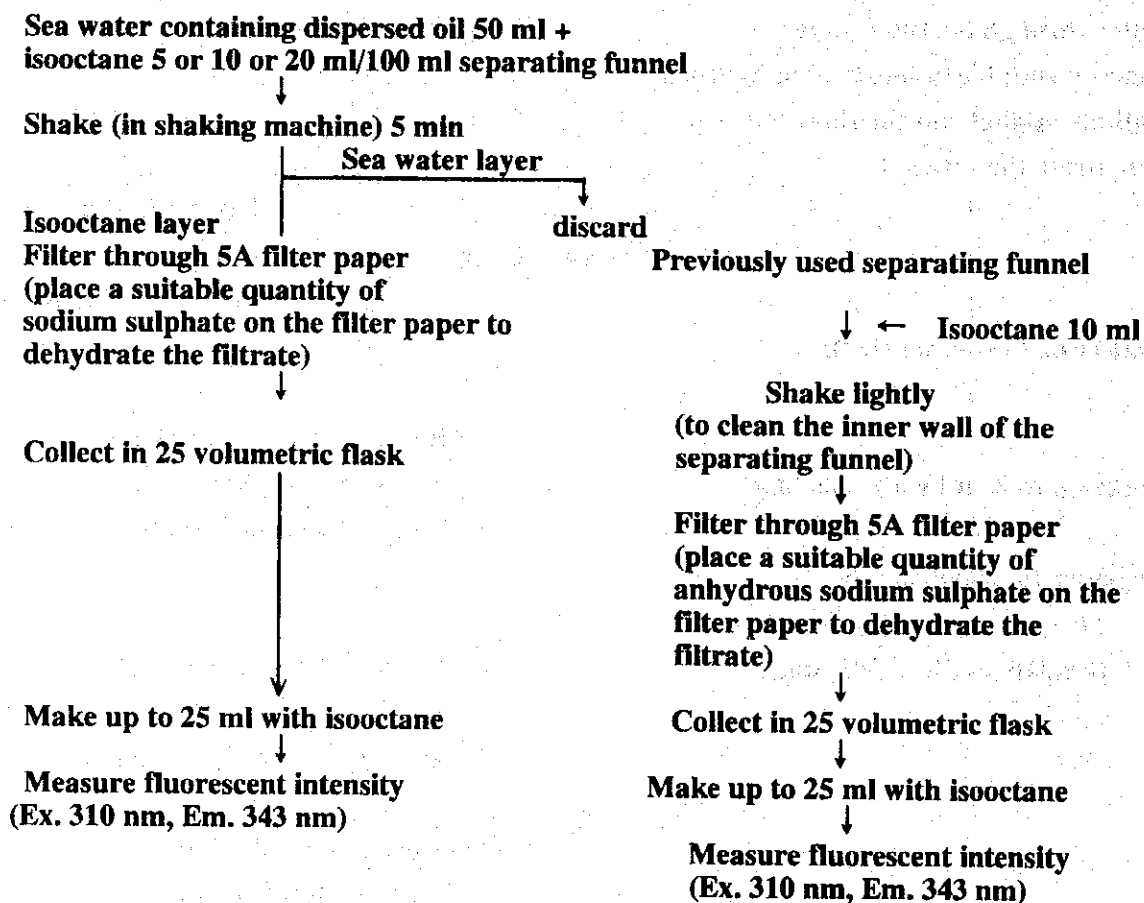


Fig. 13 Study of the necessity for cleaning the inner wall of the separating funnel after collecting the isooctane layer

(8.1.2.A)

Measurement conditions

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

(2)-4 Understanding the Blank (fluorescent intensity in sea water)

Apparatus and reagents

Fluorophotometer (Nihon Bunko FP-770)
Separating funnel shaker (Iwaki KM-Shaker V-SN)
Supersonic cleaner (Branson B 5200; 47 kHz, 120 W)
Separating funnel (100 ml)
Fuel oil A
Isooctane (Kanto Chemicals for fluoroscopic analysis)
Glass funnel
Filter paper (Advantec 5A, ϕ 11 cm)
Sea water
Anhydrous sodium sulfate (Wako special grade)
Measuring flask (25 ml)

Experimental Procedure

We measured the quantity of fluorescent material in sea water using the procedure in Fig. 14.

(8.1.2.A)

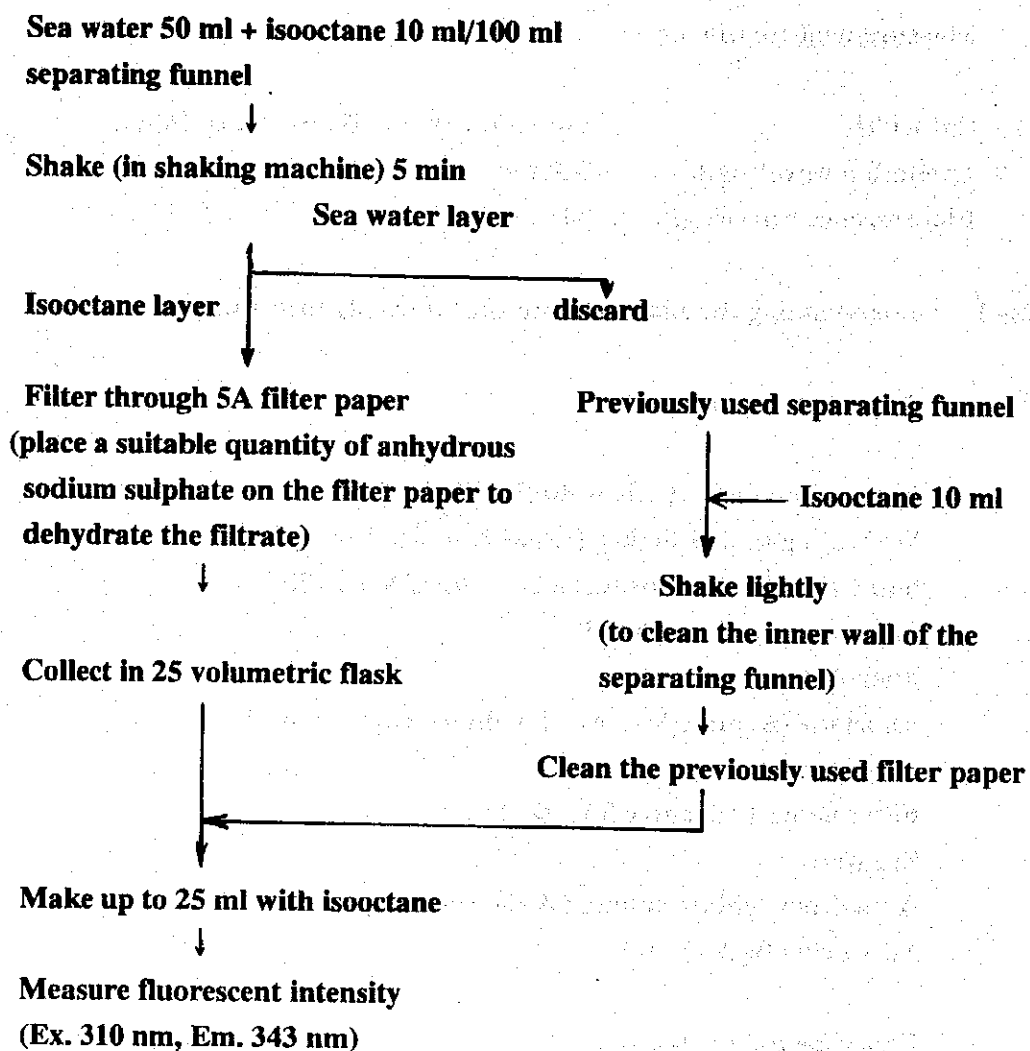


Fig. 14 Method of measuring the quantity of fluorescent material in sea water

Measurement conditions

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

(8.1.2.A)

(2)-5 **Reproducibility Check**

Apparatus and reagents

Fluorophotometer (Nihon Bunko FP-770)

Separating funnel shaker (Iwaki KM-Shaker V-SN)

Supersonic cleaner (Branson B 5200; 47 kHz, 120 W)

Separating funnel (100 ml)

Fuel oil A

Isooctane (Kanto Chemicals for fluoroscopic analysis)

Glass funnel

Filter paper (Advantec 5A, ϕ 11 cm)

Sea water

Anhydrous sodium sulfate (Wako special grade)

Measuring flask (25 ml)

Experimental Procedure

Oil content in oil-sea water dispersion was measured in accordance with the procedure shown in Figure 15. This procedure was repeated five times to investigate the reproducibility of the results. The oil-sea water dispersion was prepared in accordance with Fig. 10 "Method (2) for the preparation of oil-sea water dispersions for the study of extraction conditions".

(8.1.2.A)

Sea water containing dispersed oil 50 ml + isooctane 10 ml/100 ml separating funnel

↓
Shake (in shaking machine) 5 min.

Sea water layer
Isooctane layer
discard

Filter through 5A filter paper
(place a suitable quantity of anhydrous sodium sulphate on the filter paper to dehydrate the filtrate)

Previously used separating funnel

Isooctane 10 ml

Shake lightly
(to clean the inner wall of the separating funnel)

Collect in 25 volumetric flask

Clean the previously used filter paper

Make up to 25 ml with isooctane

Measure fluorescent intensity
(Ex. 310 nm, Em. 343 nm)

Repeat this series of operations five times.

Fig. 15 Method of measuring the oil content in sea water containing oil

Measurement conditions

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

(8.1.2.A)

(2)-6 **Comparison with TOC Method**

Equipment and reagents

Fluorophotometer (Nihon Bunko FP-770)

Separating funnel shaking machine (Iwaki KM-SHAKER, V-SN)

Ultrasonic cleaner (BRANSON B 5200; 47 kHz, 120 W)

Separating funnel (100 ml)

Fuel oil A

Isooctane (Kanto Chemicals for fluoroscopic analysis)

Glass funnel

Filter paper (Advantec 5A, ϕ 11 cm)

Sea water

Anhydrous sodium sulphate (Wako special grade)

Volumetric flask (25 ml)

Experimental procedure

The oil content in sea water containing dispersed oil was determined by TOC and by fluorophotometry in accordance with the procedure in Fig. 16 and the measured values obtained by both methods were compared. The fluorophotometry method was implemented in accordance with Fig. 15 "Method of measuring the oil content in sea water containing oil."