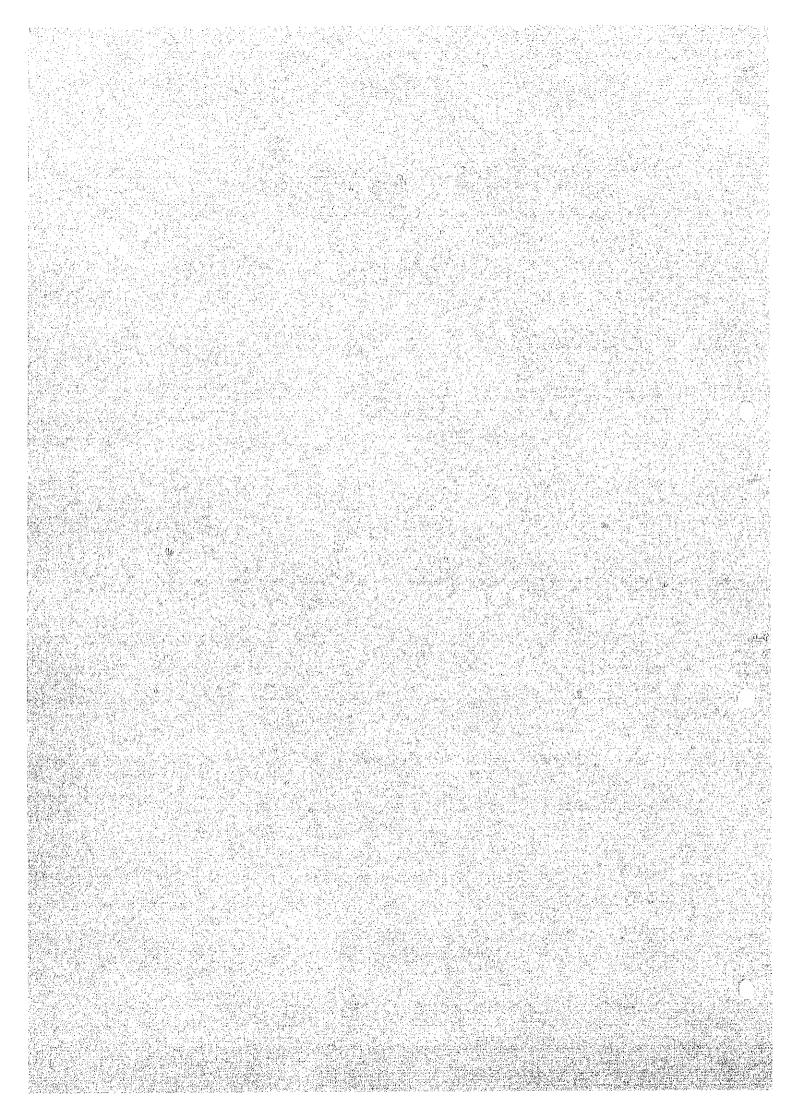
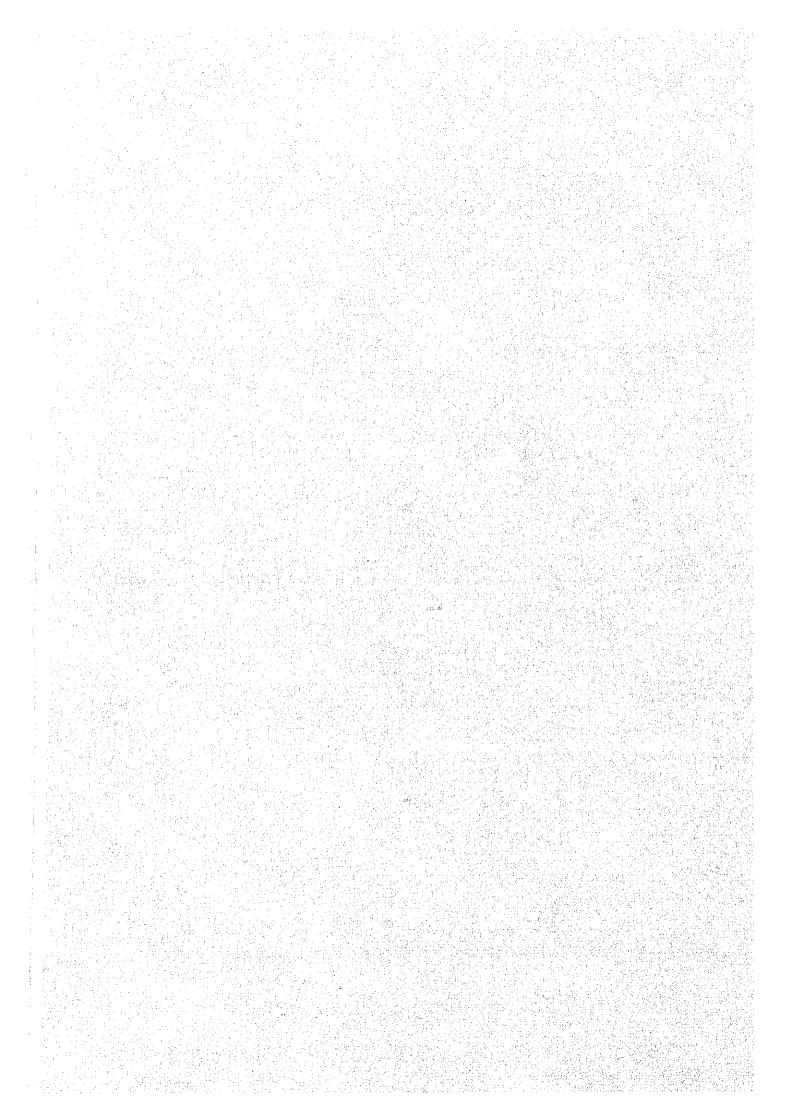
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APPENDIX RI-1



# STERILIZATION OF SEAWATER PROJECT #R1

# ONE OF JOINT PROJECTS BETWEEN SWCC AND JICA

#### JANUARY 1922

BY

HASSAN MUNSHI

SWCC RDTC, JUBAIL

SAUDI ARABIA

#### Introduction

Disinfection, literally, means free from injection. A disinfectant destroys disease for other harmful microorganisms, but not necessarily unharmful ones or ordinary bacterial spores.

Disinfection techniques can be roughly classified into two types chemical and physical. Popular chemical disinfectants for water include chlorine and other halogens, chlorine dioxide, chloramine, hydrogen peroxide and ozone.

Physical disinfection methods includes ultraviolet light, ultrasonic and ionizing radiation. The most widely used methods will be briefly described and compared.

Project RJ
B-1
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#### A: Chemical Disinfectant

#### (1) Chlorine and Chloramines

The use of reduced primary chlorination dosages and chlonamine be considered for disinfection if trihalomethanes (THM) reduction by alternative disinfection practices is desired.

The application of minimal dosages of chlorine and chloramines for primary disinfection should be evaluated on a long-term basis to guarantee adequate pretreatment disinfection and THM removal. Reduced chlorine dosages may be the only acceptable disinfection technique to reduce THMs since the Environmental Protection Agency is currently investigating toxicity of chloramines, chlorite and chlorate.

#### (2) Chlorine Dioxide

Further testing with chlorine dioxide be considered since chlorine dioxide has been shown to be unreactive to cellulose acetate membranes at concentration up to 1.2 g/m³, while minimizing THM formation. Membrane element disinfection efficacity of chlorine dioxide should be closely examined because in adequate disinfection of spiral wound membrane elements has been reported despite application of high chlorine dioxide dosages to contaminated element feed water.

Chlorine dioxide  $({\rm ClO}_2)$  is a gas at normal temperature and pressure and exists as molecular  ${\rm ClO}_2$  in pure aqueous solution. Pure chlorine dioxide is unstable and can be an explosive mixture in air at approximately eleven percent concentration (4). For that reason, it is production-site at antility. This usually is

by reaction of sodium chlorite with excess chlorine in acid solution.

$$HOC1 + H^{+} + 2 C10_{2}^{-} --- 2C10_{2} + H_{2}O + C1^{-}$$

Although disproportionation of  ${\rm ClO}_2$  to for  ${\rm ClO}_2$  and  ${\rm ClO}_3$  takes place. This reaction is much slower and, therefore, is less important from a chemical disinfectant stand point than the nearly immediate hydrolysis of molecular chlorine to hydrochlorite.

Chlorine is the most widely used disinfectant. Although it is not known exactly how chlorine destroys microorganisms, it is assumed that chlorine inhibits essential cell enzyme systems through oxidation.

Chlorine highly reactive and poisonous gas, is heavier than air and water-soluble. Dissolved in water, chlorine forms hypochlorous acid (HOCl), which in turn dissociated into only a hydrogen ion  $(H^+)$  and a hypochlorine ion  $(OCl^-)$ .

The amount of  ${\rm Cl}_2$  plus  ${\rm HOCl}^-$  plus  ${\rm OCl}^-$  in the water is known as increases its mass transfer rate from the gas to the liquid phase.

Chlorine dioxide does not react with the ammonia, but ammonia free waters do exhibit a demand for  ${\rm Clo}_2$  similar in magnitude to that for free chlorine.

#### Disinfection of Feed to Seawater RO Plants by Chloramine

Chlorination is a process where by chlorine in liquid for gaseous form (or in combination with other materials) is added to the system. The denaturing effect of chlorine on (animal or plant) microorganisms tissues forms the basis for its use as an effective water or waste water disinfectants. The disinfectant capabilities of chlorine depends on its chemical form in water which in turn is dependent on pH, temperature, organic contents of the water and other quality factors. When chlorine dissolves in water it hydrolyzes according to the reaction:

$$Cl_2 + H_2O = HOC1 + H^+ + C1^-$$

In dilute solution and at pH above 4, all chlorine will present in the form of HOCl or dissociated ions  $\mathrm{H}^+$  +  $\mathrm{Cl}^-$ .

The hypochlorous acid HOCl is a weak acid and is dissociated to hydrogen and hypochlorite ions as follows:

 $HOCl^- ==== H^+ + OCl^-$ 

This ratio between HOCl and OCl is the function of the pH, with 96 % HOCl remaining at pH 6, 75 % at pH 7, 22 % at pH 8 and 3 % at pH 9. The relationship of HOCl to pH is significant as the undissociated form appears to be the bactericidal agent in the use of chlorine for disinfection.

Sodium Bisulphate SBS Method NaHSO<sub>3</sub> Shock Treatment

The efficacy of NaHSO $_3$  as a biocide against marine microorganisms depends on exposure time, concentration of the NaHSO $_3$  and the types of microorganisms present. In general, the higher the concentration and the longer the exposure time, the greater will be the degree of disinfection. Using 30-minute exposure time, the effect of NaHSO $_3$  concentration of the degree of disinfection for sea water is given in Table 1. As can be seen from Table 1, a concentration of 50 mg/liter NaHSO $_3$  gives a very high degree of disinfection with a 30-minute exposure time.

0 <sub>3</sub> (mg/l) %Kill <sup>a,b</sup>
96
99
99.9
99.9

a: Exposure time = 30 minutes

Shock treatment for seawater RO plants should be performed for at least 30 minutes at a NaHSO<sub>3</sub> concentration of at least 500m mg/l. However, the optimum dosage of exposure time must be determined for each site.

Since biological activity is site dependent, no absolute upper limit for the biological activity can be set with respect to the need for NaISO $_3$  shock treatment. However, as a general guides if the RO feed and brine have less than  $10^3$  -  $10^4$  CFU/ml, significant biofouling would not be anticipated. Between  $10^4$  and about  $10^6$  CFU/ml, the degree of biofouling may effect the RO performance.

b: Serial dilution plating technique with Marine Agar

The shock treatment injection point should be located slightly upstream of the NaHSO3 dechlorination point. Thus, when shock treatment is applied, all areas which have carried dechlorinated water will be disinfected by the shock treatment.

anticipated. At each site the biological activity must be monitored and correlated with the overall RO performance. This will establish a historical baseline at each site with respect to biological activity. Using the baseline data, day-to-day judgments can then be made concerning significant increase (100-fold)in biological activity and the need to shock treat with NaHSO<sub>3</sub>.

#### UV Radiation Method

In this treatment system, water is disinfected by exposure to UV light at a specific intensity (dose rate) and wave length. In practice, water flows through a cylindrical stainless irradiation chamber known as a photoreactor.

In order to automate the UV disinfection process so that it operates effectively without supervision, a primary requirement is to continuously monitor the dose rate received by the feed water.

#### Copper Sulfate

The suitability and effectiveness of copper sulfate as a method of controlling plankton and algae for surface seawater RO systems are demonstrated by the successful operation of actual plants.

Four plants in addition to the Umm Lujj II plant are employing copper sulfate with Fluid Systems TFC elements. These are the 12,000 m $^3$ /d plant in Jeddah, the 500 m $^3$ /d Jeddah ship repair yard plant (1980), the 1,200 m $^3$ /d Rosarito Beach, Mexico plant (1986), and the 10,000 m $^3$ /d plant in Ras Tajura, Libya (1948). For these plants, there has been no appreciable biological fouling or growth of algae downstream of the point of copper sulfate injection.

#### Evaluate the Effectiveness of NaHSO3

Samples of the RO feed and brine for microbiological analyses should be collected prior to and after the treatment. The results from the microbiological analyses will show the effectiveness of the NaHSO<sub>3</sub> shock treatment.

If the microscopic technique is used, the effectiveness of the shock treatment will be obtained within a couple of hours of sample collection. Culturing techniques will require several days before the effectiveness of the shock treatment can be determined.

Anaerobic and sulfate reducing bacteria are more resistant to NaHSO<sub>3</sub> than aerobic bacteria. RO plants are designed to avoid dead endsand stagnant area where anaerobic bacteria can thrive. If anaerobic bacteria become a problem, off-line disinfection and cleaning can be used to kill and remove them from the RO system.

#### Home Effective ISW Disinfection

No naturally occurring microorganisms or mutants have been found which can resist inactivation by UV. Bacteria, viruses, bacterilphages, molds, protozoa, yeasts, and algae are all susceptible and can be killed or inactivated if irradiated with UV at a sufficient intensity and suitable wave length for effective disinfection. The dose rate is vitally important. Unlike chemical disinfection, however, there are no drawbacks to overdosing with UV except that it wastes energy.

#### Effect of Ultraviolet Radiation on Various Microorganisms

Different microorganisms are affected differently by ultraviolet radiation. To demonstrate this, it is beneficial to review some data. Tobin, et. have documented the resistance of various microorganisms as shown in the Table.

Resis				Microorg ion				
Bacteria legionella pueumephila	380	Micro	watts	-sec/cm <sup>2</sup>	2,760	Micro	watts	-sec/cm <sup>2</sup>
E. Coli P. aeruginesa	3,000 5,500		<u>-</u>		6,600 10,500	. ; <u>-</u> .	- -	
Spores	12,000	<del>-</del>	<del>-</del>	-	22,000	<u></u>	<u>-</u>	· •••
Viruses Influenza Tobaccomosic	3,600 240,000		- -		6,600 440,000		1	

When UV light impinge on a microorganism, it rearranges the DNA and RNA molecules of the microorganism. This blocks the microorganism's ability to replicate itself, and consequently, it ability to breed colonies. The peak region of germicidal effectiveness is the 240-260 nm UV wave length range. This is much shorter wave length than the UV light wave curve from the sun, which cuts off at about 290 nm.

#### Evaluation of the Efficiency of UV Disinfection System

- \* One problem that has been cited as serious disadvantage in the use of UV disinfection is the difficulty of measuring the UV dose. Unlike chlorination and ozonation, there is no measurable chemical residual. This makes the immediate control of the process difficult.
- \* Engineers choosing UV disinfection systems must usually rely on estimated of average dose based on insubstantiated estimates of intensity theoretical residence time.
- \* Most current UV disinfection systems employ tubular germicidal lamps enclosed in a second quartz tube submerged in a chamber through which the fluid flows.

Currently there are two major types of UV equipment. Low-pressure lamps and medium-pressure lamps being produced for the industrial market place. Due to the energy output differences of the lamps, the equipment designs are different. The low-pressure lamps system is designed as a multiple lamp system in the form of a tube bundle. The medium-pressure lamp system is designed using a single lamp in a probe form.

The low-pressure designs is used where absolute sterilization is required in such industries as pharmaceutical, food and beverage. Medium-pressure is well suited for all types of wastewater and right-turbidity applications.

#### Consideration into UV Materials:

Various factors affecting UV disinfection equipment must be taken into consideration when selecting or sizing a particular unit. Sizing application—as well as site—specific.

These factors must be considered for each application:

- \* Flow rate, both normal and peak demand
- \* Absorption coefficient (transmissionability) of the fluid being treated
- \* The type of organisms to be treated, and the associated energy levels required for the organisms
- \* Fluid composition, such as temperature, pressure, organic, inorganic, seasonal variation, scaling tendency, etc.
- \* Installation location (indoor, outdoor) and environment (wet, dry, fumes)
- \* Electrical power source available
- \* Type of operation (batch or continuous)
- \* Maintenance capability of on-site operators

Ultraviolet equipment is a tool that may be used to greatly enhance microbial control of a water treat. Size it for the task that it is to accomplish.

#### A Comparison of Chlorine, Ozone and UV

Yipand Korosewich compared UV with chlorine and ozone. Their Results are in the Figure

UV disinfection destroys common bacterial and viral pathogens more effectively than either chlorine or ozone. In figure, the dose required to destroy common pathogens is compared to E. Coli, which is the common indicate organism. It shows that UV destroys the other pathogens with essentially the same dose are required for E. Coli. Chlorine and ozone require much higher dose to destroy most of the other pathogens. A low indicator organism count using UV ensures destruction when using chlorine and ozone. The destruction of spores and cysts require much higher UV dosages.

Oxidation of organic is important in addition to disinfection. Here too, ozone excels with 52 percent higher oxidation power than chlorine and 38 percent higher than HOC1 chlorine oxidation byproducts sometimes present water treatment problems, which are reduced by using ozone. Ultra violet light alone has no oxidation power. But it can catalyze ozone or hydrogen peroxide oxidation to form hydorxyl radicals, which have 105 percent higher oxidation power than chlorine.

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## ... A comparison of chlorine, ozone and UV.

By James E. Cruver, Ph.D.

isinfection, literally, means free from infection. A disinfectant destroys disease or other harmful microorganisms, but not necessarily unharmful ones or ordinary bacterial spores. The Environmental Protection Agency and World Health regulations define. water disinfection by the absence of an indicator coliform bacteria group. On the other hand, sterilization implies complete destruction of all forms of life, which includes microorganisms. Most water we use is disinfected; medical and pharmaceutical applications require sterile water.

Disinfection techniques can be roughly classified into two types: chemical and physical. Popular chemical disinfectants for water include chlorine and other halogens,

chlorine dioxide, chloramine, hydrogen peroxide and ozone. Physical disinfection methods include ultraviolet light, fine filtration, heat, ultrasound and ionizing radiation. The most widely used methods are chlorination (including chloramines), ozonation and ultraviolet disinfection. In this article, these three methods will be briefly described and compared.

Chlorine and ozone are both chemical disinlectants. In general, chemical disinfection is a compromise between

the benefits of destroying microorganisms and the detriments of chemical toxicity and undesirable byproduct formation. Chemicals require time for reaction, and the degree and rate of reaction are strongly influenced by temperature and sometimes pH. The chemicals.not.only\_react.with\_microorganisms, but also with other suspended and dissolved materials in water. Whereas some of these chemical reactions are desirable, such as oxidation of iron, other reactions yield undesirable byproducts.

physical process that causes molecular rearrangements, products duces no undesingle hyproducts. However nolling power. Whether this limitation is a disadvantage

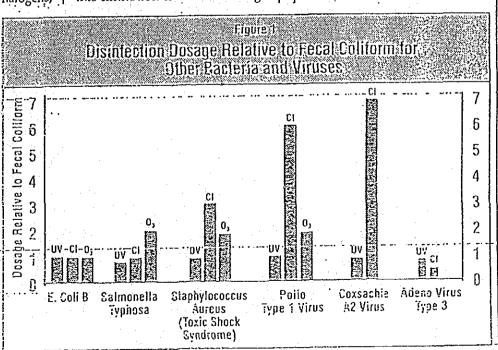
depends on the particular application. Important process variables that affect UV performance include the concentration of suspended matter and the UV light absorbance of the fluid.

#### Chlorine

Chlorine is the most widely used water disinfectant. Although it is not known exactly how chlorine destroys microorganisms, it is assumed that chlorine inhibits essential cell enzyme systems through oxidation.

Chlorine, a highly reactive and poisonous gas, is heavier than air and water-soluble. Dissolved in water, chlorine forms hypochlorious acid (HOCI), which in turn dissociates into a hydrogen ion (H\*) and a hypochlorite ion (OCI).

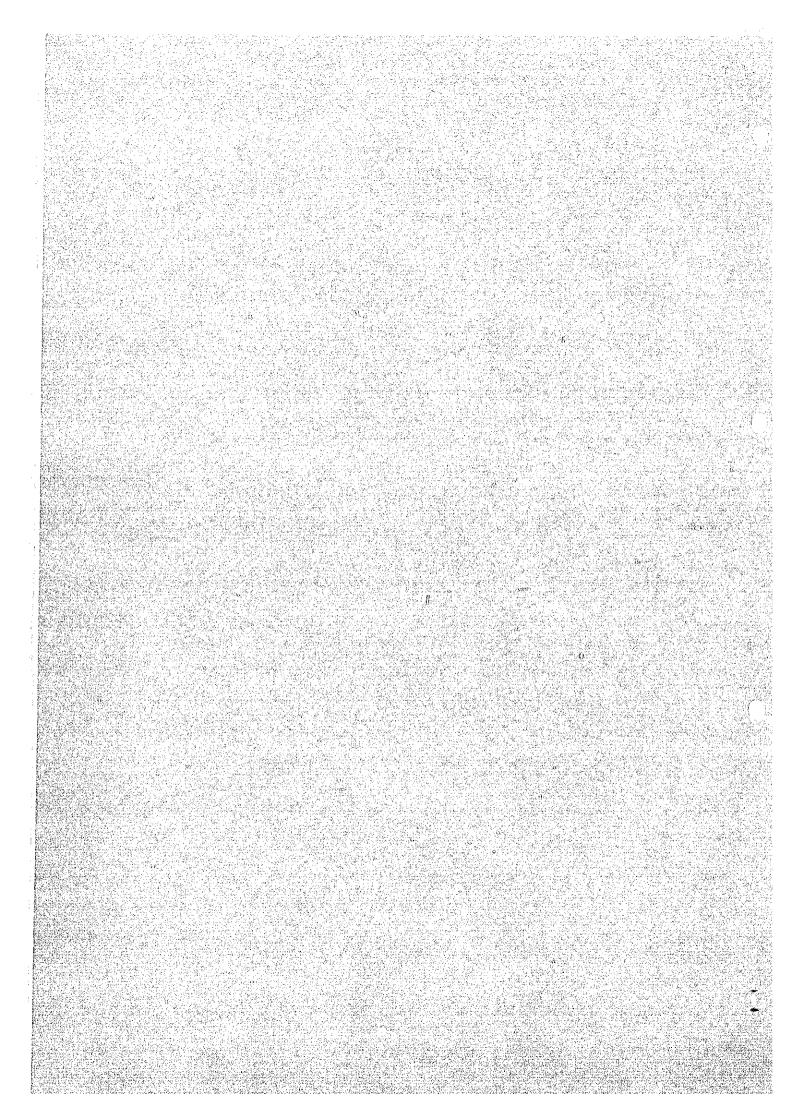
The amount of Cl<sub>2</sub> plus HOCl plus OCl in the water is known as



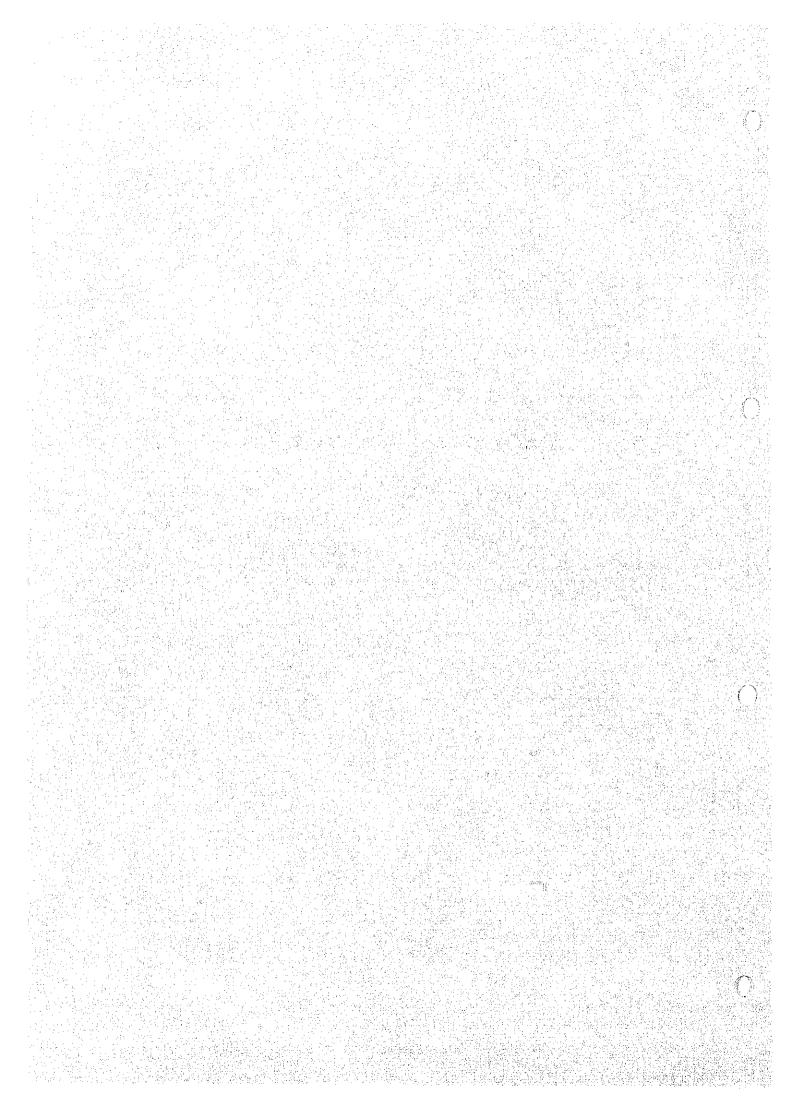
OCTOBER 1989

### 4. APPENDIX for R2 (Pretreatment of Seawater)

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APPENDIX R2-1



### APPENDIX R2-1

### PRETREATMENT SYSTEM OF SEAWATER

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- 2. Pretreatment Process
- 3. Functions of Pretreatment System
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- Fig.11 Chronological change of F1 value in treated water due to the change of coagulant (FeCl<sub>3</sub>) concentration

#### Pretreatment System of Seawater Desalination Plant

In the following section, we explain some basic points about the pretreatment system and its selection criteria.

#### 1. Purpose of a Pretreatment System

- (a) Besides soluble salt, seawater contains: microorganisms, fine sands, colloidal substances and organic matter. They may stick to membrane surfaces, thereby blocking the membranes causing (fouling). Fouling may lead to a rise in pressure loss of the reverse osmosis module, drift current, or could decrease of
- (b) Seawater contain hardening substances such as: calcium and magnesium compounds. As seawater becomes concentrated in the module, such substances may deposit on the membrane surface resulting in scaling.

The pretreatment removes turbidity and hardening substances from the feed, and hence is intended to prevent fouling and scaling.

#### 2. Pretreatment Process

membrane performance.

- (a) Criteria for the selection of a pretreatment process Raw seawater becomes turbid because of:
- (1) propagation of microorganisms (especially in spring and summer)
- (2) stirring up of turbid substances from the bottom of sea (due to storms or wave heaving, especially in fall).

#### 3. Functions of a Pretreatment System

(a) Removal of suspended matter

When turbidity is caused by fine colloidal particles, it is hard for conventional sand filtration to remove them. In such circumstances, the following methods are employed:

(i) Coagulation sedimentation....

In a pond containing flocks, coagulant is added to form larger flocks, which are to be removed in a sedimentation pond as settling sludge. This process requires a large pond and

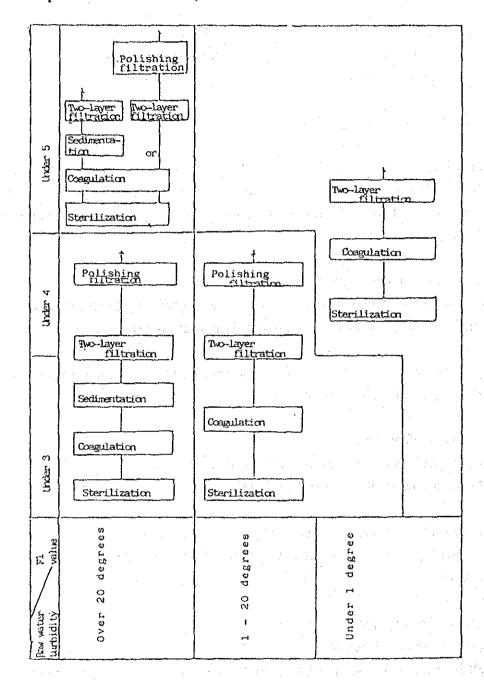


Table 1. Example of selection criteria (raw seawater/FI values)

hence is cost, this method is applied mainly to treat raw seawater with high turbidity.

#### (ii) Coagulating filtration....

Coagulant is injected into a pipe, so that flocks are formed and removed through a two-layer filter. This method is applied to raw seawater with a turbidity of 1 to 20 degrees.

(b) Prevention of chemical deterioration

- (i) When using Cellulose acetate membrane..., with improper control of feed pH, the desalting function deteriorates due to membrane hydrolysis. Hydrolysis accelerates when the pH value is over 7. To prevent this type of membrane deterioration, sulfuric acid is injected to control pH values, between 6-6.5.
- (ii) The performance of synthetic high polymer membrane (polyamide, polyether, etc.)....deteriorates through membrane oxidation decomposition caused by residual chlorine. To prevent this type of membrane deterioration, dechlorination is carried out by injecting sodium bisulfate (SBS, NaHSO<sub>3</sub>), sodium sulfite, or other reducing agent (NaHSO<sub>3</sub> + Cl<sub>2</sub> + H<sub>2</sub>O, —NaHSO<sub>4</sub> / 2HCl), it is also possible to remove chlorine using activate carbon.
- (c) Prevention of scaling
- (i) Seawater contains calcium, magnesium, iron, manganese ions and other inorganic substances. Among them, calcium (400 mg/l) and magnesium (135 mg/l) become deposited as seawater is condensed in the reverse osmosis module. Calcium carbonate, in particular, has a low solubility, and begins to be deposited when the concentration is doubled).
- (ii) In seawater, such substances exists as carbonate ions (CO<sub>3</sub><sup>2-</sup>) or bicarbonate ions (HCO<sub>3</sub><sup>-</sup>). Because relatively of it's great solubility, calcium bicarbonate is less likely to be deposited on the membrane surface. Fig.1 shows the relation between ph and carbonate, bicarbonate ions and carbonic acid.

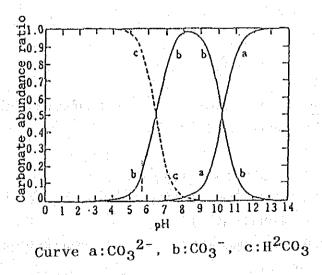


Fig.1. Relations between pH and carbonate, bicarbonate ions and carbonic acid

- (d) Prevention of slime formation
- (i) If seawater contains microorganisms, they attach themselves to the membrane surface forming slime.
- (ii) In the case of a cellouse acetate membrane, it may biodegraded by microorganisms. Since this membrane is relatively resist to chlorine, the most common method to prevent slime formation is to suppress propagation of microorganisms by keeping a certain percentage of residual chlorine in the feed, concentration (0.2-0.5 mg/l).
- (iii) In case of other polymer membranes attachment of microorganisms to the membrane leads to biofouling which affected membrane performance. Since this membrane is subject to oxidation decomposition by chlorine, it is necessary to remove the chlorine (which is injected for sterilization) by injecting sodium bisulfate in the feed just before it enters the module.

#### 4. Structure of the Filter<sup>1</sup>

(a) Criteria for selecting a filter

For the selection of a filter, the space of the plant should be taken into account as well as the performance of the filter itself. Two types of filters are employed: pressure and gravity filter. Table 2 gives comparison of a pressure type and gravity type filters. Fig.2, 3 and 4 show the structure of gravity type filter, vertical pressure type filler and horizontal two-layer filter, respectively.

#### 5. Chemical Injection<sup>3</sup>

(a) Sterilization by chlorine

Purpose: To prevent propagation of microorganisms and shellfish (purplish, barnacles, etc.) by means of sterilizing effect of chlorine

Type of chemical:

- (i) Chlorine gas (liquefied chlorine)
- (ii) Chemicals (bleaching powder, sodium hypochlorite (NaClO), calcium hypochlorite (Ca(ClO)<sub>2</sub>)
- iii) Sodium hypochlorite produced by sea water electrolysis Evaluation:
- (1) Injection of chlorine gas (i) or chemicals (ii) is not very expensive, but requires work for injection or replacement of gas cylinders. In addition, the acquisition of gas or chemicals is rather expensive.

Table 2 Comparison of Pressure Type Filter and Gravity Type Filter

· ·	Pressure Type	Gravity Type
	Two-Layer Filter Horizontal, Cylinder	Two-Layer Filter
Structure		Horizonal, Semi-under- ground
Material	Steel, rubber lining	Concrete
Filter media	Sand + anthracite	Sand + antheracite
Filter speed	8 - 15m/hour	5 - 8m/hour
Pressure loss	8 - 10m	2 - 3m
Filtering area	a Small	Large
Filtering	Reasorable	Good
performance		
Backwash	Once/day	Once/day
Backwach method	Air + water + rinse	Air + water + rinse
Backwash	30 - 36m/hour	30 - 36m/hour
speed		
Backwash	Filtered water	Filtered water
water		
maintenance	A little complicated	Simple
Character- istics	<ol> <li>Filtering speed is high and installation space is small</li> </ol>	1. Filtering speed is low and installation space is large
	2. The amount of air and water required for backwash is small	2. The amount of air and water required for backwash is large
	3. In a large plant, a relatively large number of filtering units is required because of limited dimensions	3. Less power is required
	4. Installation can be done unit by unit during the construction period	4. Filtered water has good quality
		5. Because of monolithic structure, installa- tion cannot be divided.

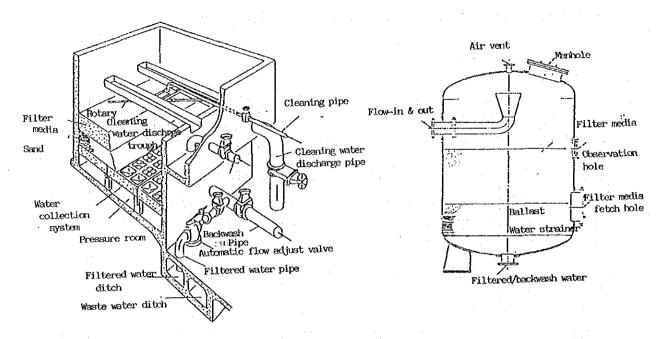


Fig.2 Stucture of gravity type filter

Fig.3 Structure of vertical pressure type filler

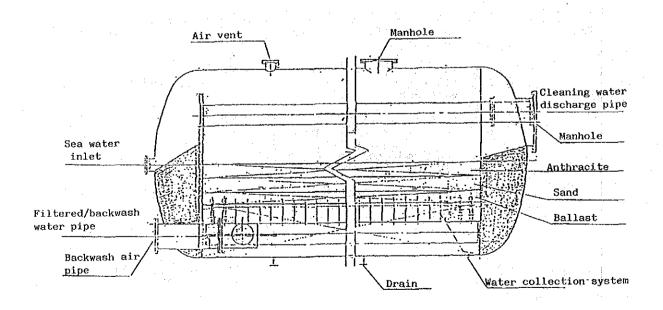


Fig.4 Structure of horizontal two-layer filter

(2) The use of sodium hypochlorite produced by seawater electrolysis (iii) requires a chlorine generator, and hence the initial installation cost is high. Nonetheless, compared with the injection of gas or chemicals, this method has advantages such as simple maintenance and low operation cost. In a large plant, it is common to install a chlorine generator.

(b) Coagulant

Purpose: To coagulate and remove very small colloidal particles by injecting a coagu-

lant chemical

Type of chemical: (i) Aluminum salt; (ii) Ferric salt

Evaluation: As coagulant for sea water, ferric salt (ferric chloride (FeCl<sub>2</sub>), etc.) is more

advantageous than aluminum salt.

(c) pH control

Purpose: To suppress the pH value of raw sea water (approx.8.2) down to 6.0 to 6.8 in

order to prevent the hydrolysis of the cellulose type membrane as well as to prevent the scaling of the membrane surface. Normally, acid destroys the

calcium carbonate preventing calcium carbonate type scaling.

Type of chemical: (i) Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>); (ii) Hydrochloric acid (HCl)

Evaluation: As far as performance is concerned, there is little difference between sulfuric

acid and hydrochloric acid. However, sulfuric acid is more commonly used,

because it is easier to handle and less expensive.

#### 6. Comparison of Coagulants

(1) Coagulating Effect

Table 3 shows a comparison of ferric and aluminum salts, both of which are widely used for water treatment.

Because of the pH value of sea water (approx.8.2), ferric salt, which has a wider pH range, is more suitable than aluminum salt as coagulant for sea water.

Figs. 5-8 shows detailed comparison of ferric salt and aluminum salt according to the magnitude of pH values. As seen from Figs, in the vicinity of pH 8, ferric salt coagulant have better effect than aluminum salt coagulant.

Advantages of ferric salts coagulant are as follows:

(a) The formation of flocks (hydroxide) is quick. Flocks are relatively large and hence have greater sedimentation velocity.

Table 3 Comparison of Fe and Al salts as coagulants

		7 / 7 7 7	Aluminum
Appli- cable		Iron (II)	sulfat
	Coagulant		4 5 40 5 9 4 3 6 0 6 1
0	Solubility of hydrolysis products (g/100ml)	4.8 x 10 <sup>-9</sup> (18°C)	
	Hydrolsis constant	2.5 x 10 <sup>-3</sup>	1.05 x 10 <sup>-5</sup>
0	Solubility product	1.3 x 10 <sup>-22</sup>	3.9 x 10 <sup>-11</sup>
0	Hydroxide specific- gravity	3.3 - 3.9	2.42
0	pH range	4.0 - 11	6.0 - 8.5
	Optimum pH range	6.1 - 7.4	6.0
0	Chemical injection rate	Small	Medium
0	Sludge compression rate	Good	Bad
0	Sludge dehydration	Good	Normal
0	Leaching of phosphorus from sludge	Minimum	
0	Affinity with phosphorus	Maxmum	- <del>-</del>
0	Cost	Low	Normal

- (b) Flocks (hydroxide) have greater compressibility.
- (c) The range of optimum pH value is wide.
- (d) Sludge has excellent dehydration property.
- (e) Once sedimented, hydroxide is not dissolved easily.
- (f) The operating cost is relatively low.

Comparison of pH Ranges for Coagulation of Al Salt and Fe Salt in River Water

#### Testing method:

Jar test: Quick agitation 100 rpm/min.

Slow agitation 60 rpm/10 min.

Stationary state 5 min.

Figs. 5-8 show the supernatant turbidity and residue amount after the stationary state.

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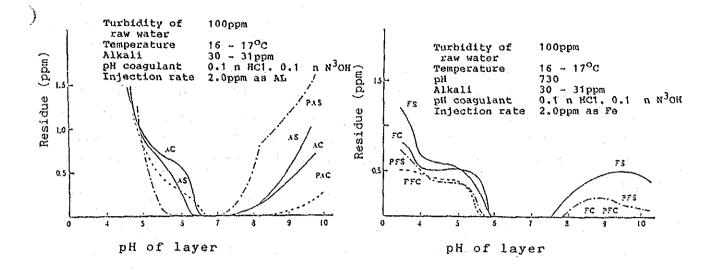


Fig.5 Coagulate pH range of Al salt in river water

Fig.7 Coagulate pH range of Fe<sup>3+</sup> salt

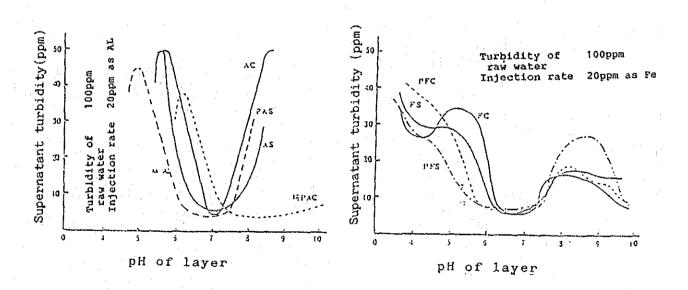


Fig.6 Coagulate pH range of Al salt in river water

Fig.8 Coagulate pH range of Fe3+ salt

As for optimum pH values for coagulation with Al salt is pH 6-7 when using polyaluminum sulfate (PAS), and pH 6-8 with PAC coagulant. In the case of Fe salt, the pH range for coagulation is around 6-8 regardless of types. Thus, Fe salt has a wider pH range than Al salt.

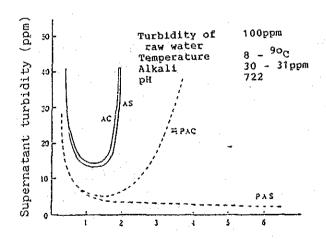
As for the removal of turbidity, too, once out of the neutral range, Al salt's effect become extremely small. On the other hand, Fe salt has excellent effect for removing turbidity in a wider pH range.

#### (2) Practical Aspects

For the evaluation of coagulants, not only coagulating effect, but also the allowable range of the optimum injection rate should be taken into account. Such range is important for the safety of handling coagulants.

Figs. 9-10 show the coagulating effects of Al and Fe salt according to the injection rate.

As seen from the figures., the Fe salt coagulant show stabler effect in a wider injection range than the Al salt coagulant.



Turbidity of 100ppm raw water Temperature 8 - 90C Alkali 30 - 31ppm 722

Fig. 9 Comparison of coagulating effect of Al salt and basic salt

Fig. 10 Comparison of coagulating effect of Fe<sup>3+</sup> salt and basic salt

- (3) Considerations for Using Fe Salt Coagulant
- (a) Because of its acid nature and hence the possibility of corrosion, attention must be paid to the

materials of machines and equipment.

- (b) Disposal of waste water (coagulation water, backwash water, etc.) becomes necessary.
- (c) Attention must be paid to the handling of coagulant fluid.

## (4) Criteria for the Injection Rate of Coagulant

Fig.11 shows FI values of treated water and the filter pressure losses measured against the change of coagulant (ferric chloride: FeCl<sub>2</sub>) concentration.

When the Fe concentration is 0.5 mg/l, the FI value of treated water is less than 4. As the concentration increases, although the turbidity-removing effect improves, the filter pressure loss also grows large. For the pretreatment in the RO system, the optimum concentration may lie around 1.0 mg/l.

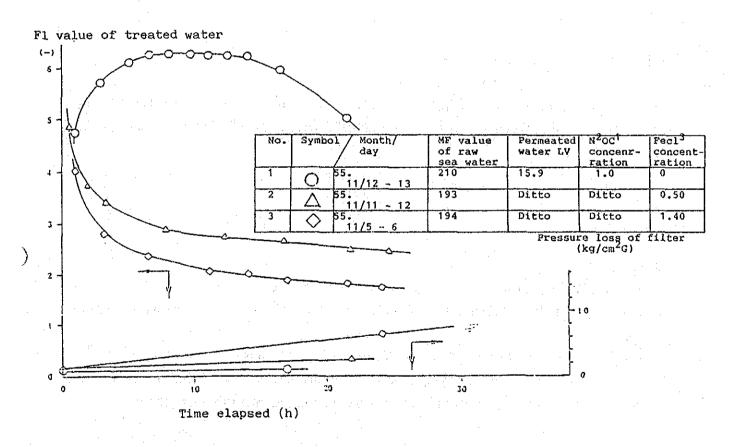


Fig.11 Chronological change of F1 value in treated water due to the change of coagulant (FeCl<sub>3</sub>) concentration

## Example of the Effect of Coagulation Injection<sup>4</sup>

Without coagulant injection, but with filtration:

Quality of treated water: The FI value of treated filter water is 4.5-6.2, which is not much different from that of raw sea water. Thus, filtering effect is almost null. Pressure loss of the filter...Less than 0.01 kg/square cm/day

With coagulant injection (0.5 mg/l, Fe), and filtration:

Quality of treated water: From the initial seawater FI value of 4.8-3.5, FI drops to less than 2.5 and stays at 2.5-3 after the clapse of five or six hours. Pressure loss of the filter is less than 0.35 Kg/square cm/day

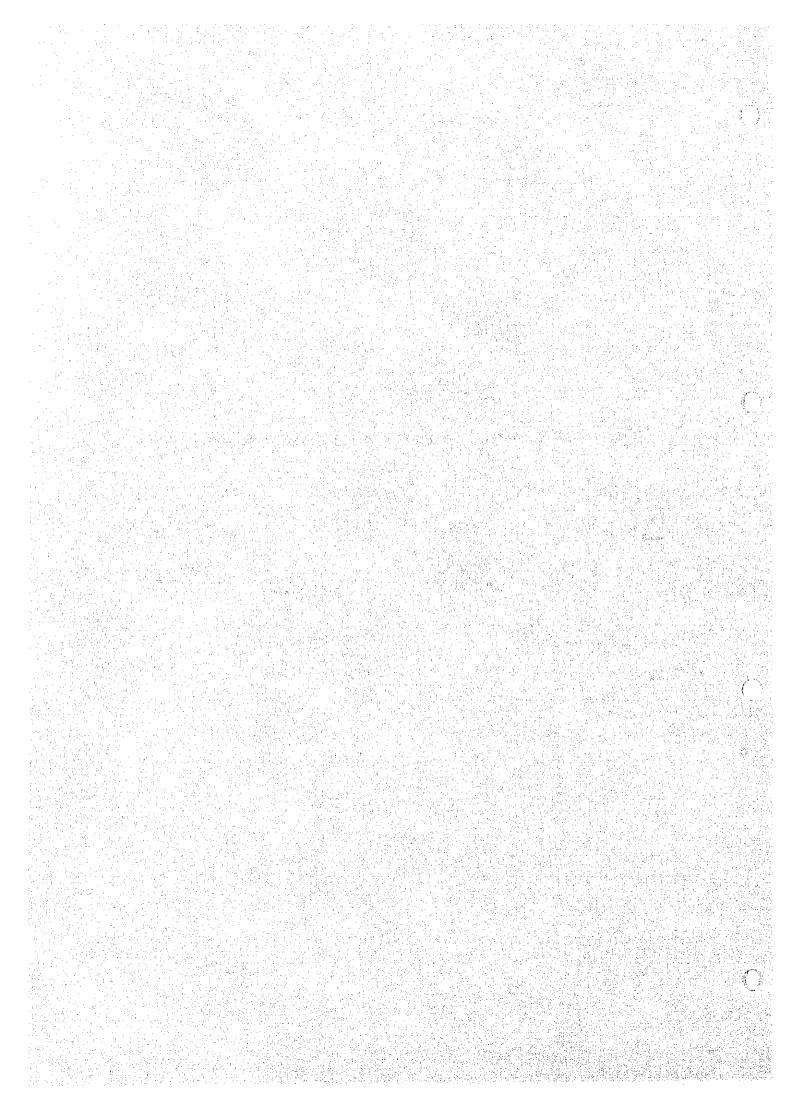
With coagulant injection (1.4 mg/l, Fe):

Quality of treated water: From the initial value of 4.0-3.0, FI finally becomes less than 2.0. and stays at 2.0-2.5 after the elapse of five to six hours. Pressure loss of the filter is less than 0.6 Kg/square cm/day.

#### References

- 1. Technical Report, Mitsui Engineering & Shipbuilling Co., Ltd.
- 2. "Everything in Water Science and Water Re-use Technology", Water Re-use Promotion Center
- 3. "Coagulants for water treatment", Taimev Chemical Co. Ltd., press
- 4. "Technical Report on Energy Saving Seawater Desalination in 1980", Ministing of International Trade and Industry, Industrial Location and Environ, Mental Protection Bureau.

APPENDIX R2-2



Measuring Technology of Oil in Seawater

Instruction Manual of OIl Content Analyzer OCMA-220

Instruction Manual
OCMA-220
Oil Content Analyzer

Horiba, Ltd. Kyoto, Japan

# Table of Contents

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## 1. Description

The OCMA-220 is designed to measure quickly and precisely, the organic hydrocarbon contamination in fresh or salt water samples. The hydrocarbons may be present in the sample water in the form of oils, fats, greases or waxes.

A nondispersive infrared (NDIR) analyzer is used to measure the concentration of hydrocarbons in the solvent solution. This technique closely approximates several standard methods in which the oil is extracted with a solvent, which is then analyzed by infrared spectrometry or weighed.

The OCMA-220 is a portable, precise instrument ideally suited for quickly analyzing the oil content of ballast and bilge water and the hydrocarbon contamination in industrial plant waste water effluent or incrivers, lakes and oceans.

The instrument consists of two sections; a sampling handling section, and an analyzer section. Both sections are contained in one portable housing. The oil content is read directly in ppm oil on a digital panel meter.

All accessories necessary for the operation of the OCMA-220 are included in the shipping kit except the extraction solvent which must be obtained by the operator. The ship kit includes:

20ml syringe for sample 1
20m2 syringe for solvent 1
25µl microsyringe for calibration l
Heavy oil for calibration (10ml bottle) 1
Water/oil filters 5
200ml beakers 4
Fuse
Power cord (2.4m) 1
Philips screw driver 1
Instruction manual
Instruction label 1

2. Specifications

2.1 Specifications

Principle : Solvent extraction, NDIR analysis

Ranges :  $0 \sim 5$ ,  $0 \sim 20$  ppm (dual ranges)

Measuring object : Organic hydrocarbon contamination in fresh or salt water

sample

Data display : Liquid crystals, 3-digit panel meter

Repeatability : 0 ~ 20 ppm: ±2% of full scale ±1 digit

0∿5 ppm : ±4% of full scale ±1 digit

Calibration : Known oil/solvent mixture for span calibration; pure sol-

vent for zero

Sample volume : (A) 0 ~ 20 ppm: 15ml per measurement

(B) 0 ∿ 5 ppm : 20ml per measurement

Solvent : Flon S-316 (Fluorochlorocarbon)\*\*

Solvent volume : (A) 0 ~ 20 ppm: 15m2 per sample

(B) 0 ∿ 5 ppm : 10ml per sample

Extraction : By built-in extractor

\* Externally extracted samples may also be measured.

Ambient temperature: 0 ~ 40°C

Output : O ~ 100mV DC

Power requirement : AC line voltage, 50 or 60Hz to be specified, approx. 50VA

Dimensions :  $220(W) \times 362(D) \times 375(H)$ mm

 $[8.7(W) \times 14.3(D) \times 14.8(H) \text{ inch}]$ 

Weight : Approx. 10kg (22 1b)

\*\* Other kind of solvent such as carbon tetrachloride may be used, but the analyzer must be adjusted (including optical alignment) for proper operation.

## 2.2 Contents of standard package

	Item	Q'ty	Appearance
1	OCMA-220	1	
2	Syringe for solvent (20ml)	1	- Aumin Daniel
3	Syringe for sample (20m½)	1	Junio Juliano
4	Microsyringe for calibration (25μ£)	· · · · · · · · · · · · · · · · · · ·	
5	Glass beaker (200ml)	4	
6	Heavy oil calibration (10m£)	1	
7	Water/oil filter	5	

	Item	Q'ty	Appearance
8	Fuse For 100 ∿ 115V AC area: 1A For 220 ∿ 240V AC area: 0.5A	1	
9	Phillips screw driver	1	
10	Power cord For North America: A For Europe : B	1	A SD B B
11	Instruction manual	1	OCMA-220 Instruction Hanual
12	Instruction label	. t.	

## 3. Principle of Operation

#### 3.1 General

Oil is generally a mixture of many different hydrocarbon compounds which exhibit widely diverse chemical properties. Because any two oil samples may contain different concentrations of these hydrocarbon compounds, the results of an analysis of water samples for oil content may depend upon the method of analysis used.

Two distinct characteristics common to most oils are: (1) they are composed of hydrocarbons, and (2) they are insoluble in water. The OCMA-220 utilizes these two characteristics to allow an accurate measurement of oil in water regardless of the type of composition of the oil in the sample.

The hydrocarbon compounds contain CH radicals. Each of these radicals exhibits a very distinct energy absorption band in the range of 3.4 to 3.5 microns in the infrared spectrum (refer to Fig. 3-1). This absorption band is almost identical for any type of oil. Consequently, when the infrared absorption of an oil sample is measured between 3.4 and 3.5 microns, the absorptivity varies in direct proportion to the concentration of oil in the sample.

Because water also absorbs energy in the infrared ban between 3.4 and 3.5 microns, it is virtually impossible to measure low concentrations of oil in a water sample. Therefore, the oil dispersed in the water must be separated from the water before it can be accurately measured.

Halogenated solvents may be used to separate the oil from the water for subsequent infrared analysis because: (1) these solvents are almost insoluble in water, (2) they have a specific gravity heavier than water, (3) they readily dissolve all volatile or nonvolatile organic compounds, and (4) they do not absorb infrared energy in the 2 to 4.5 micron band (refer to Fig. 3-1).

This method provides a number of advantages over other methods used for the analysis of oil and grease in water. These include preservation of volatile components in the sample, specificity to hydrocarbons, lack of interference from suspended solids and colored substances, and good precision.

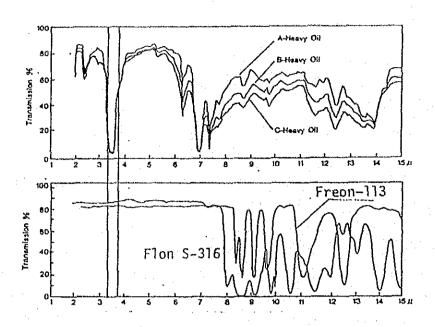


Fig. 3.1 Infrared Ray Spectrum of Heavy Oils and Flon S-316

#### 3.2 Sample handling section

The sample handling section of the OCMA-220 is a compact, efficient solvent extraction system which separates the oil from the water in the sample to be analyzed. The basic steps in the extraction process are as follows.

The operator measures xml of hydrocarbon-contaminated water with a syringe and injects the sample into the extractor chamber of the OCMA-220. The operator then adds yml of solvent.

The sample and solvent are mixed together for about one minute by the built-in agitator in the extractor chamber. After the sample is mixed, it is allowed to set for approximately one minute to allow the solvent, which now contains the oil, to settle to the lower portion of the chamber.

After the solvent has separated from the water, a valve is opened manually to allow the solvent and oil to flow into the analyzer sample cell through a filter membrane. This filter prevents water the solids from entering the sample cell and causing an error in the analysis. After the sample cell has been filled with the solvent/oil mixture, the measure switch is depressed and the reading in ppm oil is taken from the digital panel meter directly. After the meter has been read the measure button is turned off and the discharge valve on the extractor is opened to allow the system to drain.

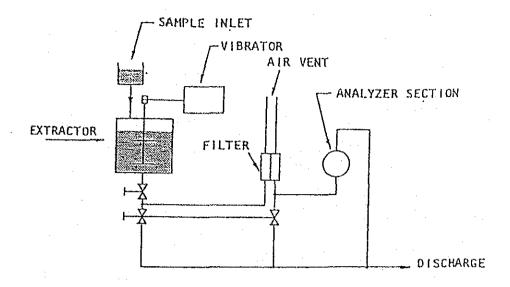


Fig. 3-2 Flow Diagram; OCMA-220

#### 3.3 Analyzer section

The analyzer section of the OCMA-220 provides the stability and accuracy inherent in a differential measurement based on the principle of infrared energy absorption. The instrument utilizes a double-beam optical system which measures the amount of oils in a sample cell and compares that value to the response from a cell filled with reference gas. A simplified functional diagram is shown in Fig. 3-3.

Two infrared sources are used, one for the sample energy-beam, the other for the reference energy-beam. The beams are blocked ten times per second by the light chopper, a two-segmented blade rotating at five revolutions per second. In the unblocked condition, each beam passes through the associated cell and into the detector.

The sample cell is a flow-through tube that receives the liquid sample to be measured from the sample handling section of the instrument. The reference cell is a sealed tube filled with a reference gas. This gas is selected for minimal absorption of infrared energy of those wavelengths absorbed by the sample component of interest.

The detector consists of two sealed compartments separated by a flexible metal diaphragm. Each compartment has a window of a synthetic crystal to permit entry of the corresponding energy beam. Both chambers are filled to the same subatmospheric pressure with HC vapor. Use of this substance as the gas charge in the detector causes the instrument to respond only to that portion of net difference in energy due to the presence of the measured component.

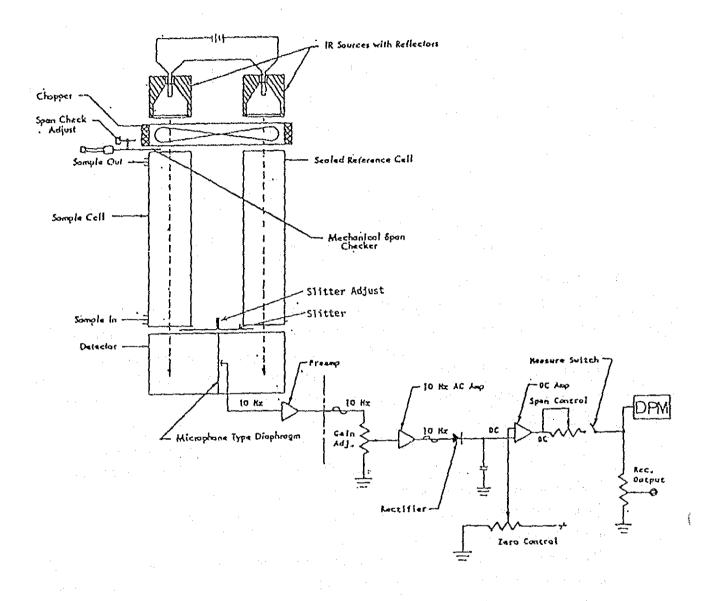


Fig. 3-3 Analyzer and Amplifier Diagram

In operation, the presence of the infrared-absorbing HC in the sample stream causes a difference in energy levels between the sample and reference sides of the system.

This differential energy increment undergoes the following sequence of transformations:

- 1. Radiant energy: In the sample cell, part of the original energy of the sample beam is absorbed by the HC. In the reference cell, however, absorption of energy from the reference beam is negligible.
- 2. Temperature: Inside the detector, each beam heats the gas in the corresponding chamber. Gas in reference chamber is heated more, however, since energy of the reference beam is greater.
- 3. Pressure: Higher temperature of gas in the reference chamber raises pressure of this compartment above that of the sample chamber.
- 4. Mechanical energy: Gas pressure in reference chamber distends diaphragm toward sample chamber. The energy increment is thus expended in flexing the diaphragm.
- 5. Capacitance: The diaphragm and the adjacent stationary metal button constitutes a two-plate variable capacitor. Distention of the diaphragm away from the button decreases the capacitance.

When the chopper blocks the beams, pressures in the two chambers equalize and the diaphragm returns to its undistended position. As the chopper alternately blocks and unblocks the beams, the diaphragm pulsates thus changing detector capacitance cyclically. This changing of the detector capacitance at a 10Hz rate is converted to an electrical signal and is routed to the preamplifier which is mounted on the detector. (Refer to Fig. 3-3.)

The preamplifier converts the signal which is very small and of a high impedance into a larger signal of low impedance. The signal is then routed to the first stage of the amplifier through the Gain Control Potentiometer. This potentiometer adjusts the gain of the overall system by attenuating amplifier input signal appropriately. The resultant attenuated signal is fed into the input of the AC operational amplifier where it is amplified. The output from the AC amplifier is then rectified and filtered prior to being sent into the DC amplifier. The DC amplifier then drives the output meter an amount directly proportional to the concentration of oils in the sample so that the concentration of oils is read directly from the front panel meter in ppm oil.

A metal "slitter" is provided in the optical system to allow the IR radiation in either the sample or the reference cell to be partially blocked by a manually adjustable amount. With the slitter centered so as to block no IR radiation

from either IR source element and with a zero standard in the sample cell, the IR intensities in each cell would ideally be equal. Due to small variations in IR sources, cell wall reflectivity and optical window transmissive properties, these intensities will likely be slightly in equal resulting in an output signal from the detector and an upscale reading at the meter. In adjusting the slitter, the sample and reference intensities are first balanced, resulting in a minimum output signal. The slitter is then moved slightly so as to block slightly more sample cell radiation (or slightly less reference side radiation) This imbalance results in an upscale signal which is compensated for electrically. Electrical zero biasing is provided by the zero adjust network shown in Fig. 3-3. It applies an adjustable zero-biasing signal to the input of the DC amplifier.

A recorder output is provided by means of an adjusting potentiometer to set the output at  $0 \sim 100 \text{mV}$  for a full scale reading.

#### 4. Installation

#### 4.1 Location

9

To insure proper performance of the instrument, choose a location that will meet the following conditions as closely as possible.

- 1. Area should be free from excessive dust or moisture exceeding 80% R.H.
- 2. Area should be free from corrosive gases.
- 3. Location should not be subject to shock or vibration.
- 4. The instrument should not be subjected to direct sunlight or radiant heat, and rapid ambient temperature fluctuations should be avoided. Environmental temperature range should be maintained between 32°F (0°C) and 104°F (40°C).
- 5. Allow for adequate air circulation around the analyzer.
- 6. Since the analyzer section and the electronics cannot be air-purged, keep the instrument away from combustible gases.
- 7. <u>Sufficient ventilation</u> must be provided to prevent breathing of carbon tetrachloride vapor (or excessive breathing of Flon S-316 vapor). A fume hood is the desired location for the analyzer.
- 8. DO NOT install the instrument near electrical equipment which causes power source disturbances (radio frequency, furnaces, electric welders, etc.), and DO NOT connect the instrument's power line to the same power source used by such equipment.
- Make the proper grounding. Be sure to locate the ground away from any potential fluctuation which could be caused by an electric heavy device...
- 10. Solvent may vary depending on production lot in its indication level (zero point). Hence solvents which were produced in different lots are to be used, pour expected amount of solvents to be used into a clean glass container for equalization of zero point level. Apply same zero point solvents both for span and measurement.

#### 4.2 Power source

#### 4.2.1 Power requirements

The power source required for the instrument is 115V (105V-125V) AC with a frequency of 60 or 50Hz. The actual frequency must be specified. (240V AC power is optional.)

#### 4.2.2 Power cord

A 2.4 meters (eight-foot) power cord, equipped with a three-prong plug (for 115V version) or European plug (for 240V version) is provided with the OCMA-220. Before connecting power cord to the power outlet make sure all power switches are in the "OFF" position.

#### 4.3 Output

The analysis can be recorded on a  $0 \sim 100$ mV potentiometric recorder by means of the recorder output jacks located on the back of the analyzer.

#### 4.4 Grounding

When 3P power outlet with a grounding terminal is available as power source, the grounding terminal on the back panel need not be connected. With 2P power outlet (without grounding terminal), however, the grounding terminal must be connected to the earth through grounding wire. Grounding work must be provided in compliance with a required standard. If such grounding work is impracticable, connect the grounding terminal to a properly grounded water pipe or a steel frame

Caution "Water piping containing vinyl chloride pipe cannot be used for grounding electrode.

- ° Do not use gas piping for grounding electrode.
- \* Use AWG20 or thicker wire for grounding wire.

## 5. Operating Controls and Adjustments

① Digital display
Digitally displays oil concentration. The display flickers for the concentration above full scale. The selected range is indicated by the mark - ...

## (2) Check button

The check button controls a preset mechanical device which partially blocks the sample beam and allows the operator to make a quick check on the overall sensitivity of the analyzer without having to use standard samples.

## ③ Span adjust

The span adjust is used to set the upscale standardization point. With a standard sample in the sample cell the span adjust is set for correct meter reading.

## 4 Zero adjust

The zero adjust is used to set the zero point (downscale standardization point). With a blank sample (pure solvent) in the sample cell, the zero adjust is set for a zero reading on the meter.

## (5) Power button

The power button controls the electronic circuitry. The OFF (down) position removes all power from the analyzer and the sample handling.

#### (6) Range selector

Selects measuring range (5 ppm or 20 ppm). (Full scale output and range lamp are switched.)

#### (7) Measure button

The measure button controls the output and meter circuits to prevent damage to the meter when changing samples or filling the sample cell.

After the cell has been filled with zero or standard solution or sample, the measure switch is switched to the ON position to take the reading. After completion of the reading the measure button is turned OFF.

# 8 Sample inlet Sample and extraction solvent are injected through this inlet.

# (9) Range lamp (5 ppm) Lights when 5 ppm range is selected. Confirm sample volume (15m2) and ex-

traction solvent volume (10m2) before injection.

- (1) Range lamp (20 ppm)

  Lights when 20 ppm range is selected. Confirm sample volume (15ml) and extraction solvent volume (15ml) before injection.
- ① Extractor chamber
  0il is extracted from sample into the solvent here.
- Description (2) Extractor valve controls the flow of sample from the extraction chamber to the analysis cell; the valve is left in the closed position until the extraction process has been completed. The valve is then placed in the open position for the balance of the analysis and the draining of the system.
- Extraction timer
  This is for setting extraction time.
- ① Discharge valve

  The discharge valve is used to drain the sample from the analyzer after completion of analysis.
- (b) Discharge outlet
  When solution overflows or when discharge valve is set to open it drains
  through this outlet.
- (b) Extractor button
  This button activates the agitator in the extractor chamber (visible through the Monitor Window). When the extractor switch is turned ON, the agitator is activated and the extractor lamp is lit. The agitator is controlled by a timer and will continue to operate for 40 seconds, 1, 2, 3, 4 or 5 minutes after which time the indicating lamp will go out and the agitator will stop.
- Recorder output adjust control
  This is for controlling full scale output of instrument.
- (B) Recorder output terminal
   DC voltage output (full scale 0.1V)
- (9) Grounding terminal Terminal for grounding
- ② Fuse
  Power fuse

Power inlet Connect supplied power cord to this inlet.

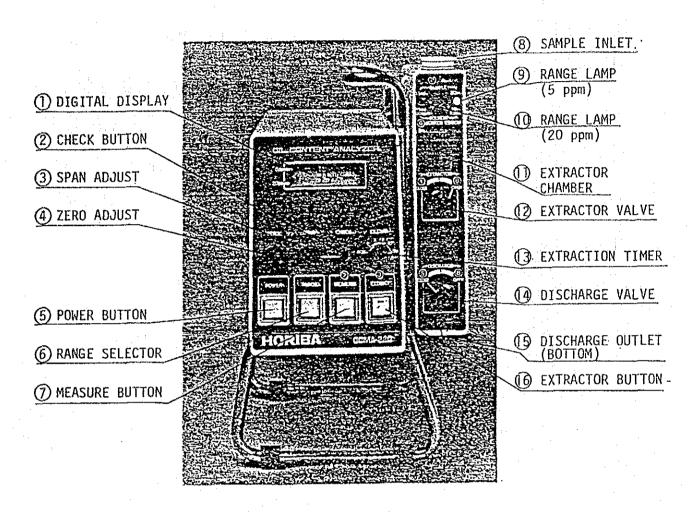


Fig. 5-1 Location of Operating Controls

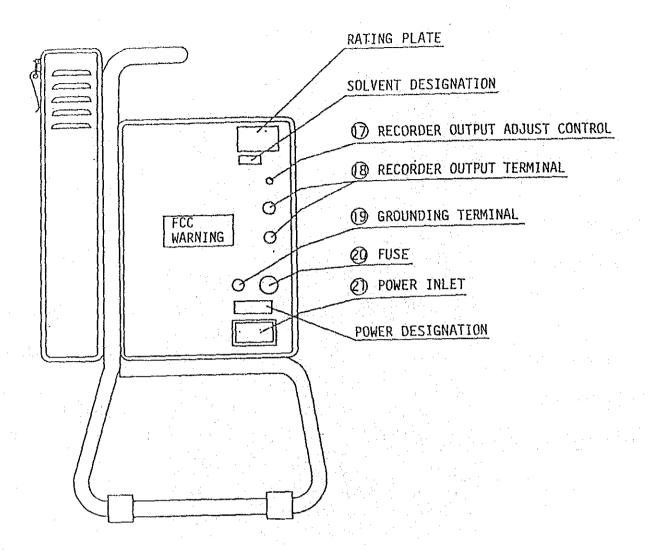


Fig. 5-2 Rear View

#### 6. Preparation for Use

- (1) Installation
  Select proper location for installation with reference to requirements for location in Section 4.
- (2) Check of grounding
  Check that grounding is properly provided, with reference to the requirements for grounding in Section 4.
- (3) Preparation of apparatus and solvent
  Place beaker under discharge outlet to receive waste solution. (Tominimize evaporation of solvent in the waste solution, pour tapping water in the beaker to the level of about lcm from the bottom.)
  Prepare syringes (for solvent and sample) and extraction solvent which meets the instrument specifications (carbon tetrachloride or Flon S-316).
  Prepare span solution for upscale standard calibration.
  Refer to the description below for the process of preparing span solution.
  - Caution Carbon tetrachloride is a toxic solvent. Users are cautioned to avoid skin contact or breathing of the vapors. Flon S-316 has relatively low toxicity. However, precautions must be taken to ensure the working area is properly ventilated when using the solvent. In all cases, the use of a laboratory venting hood is recommended. Proper care must be used in the disposal of waste solutions. The Horiba reclaimer can serve as a safe deposit for the spend solvent.
- .(4) Cleaning of apparatus

  Rinse syringes two or three times in clean extraction solvent before use.
- (5) Power ON

  Insert plug into the specified plug socket after confirming that "POWER button" and "MEASURE button" on the instrument front panel are in OFF positions (buttons protrude).

[Preparation of Span Solution (for reference)]

\* Introduction HORIBA OCMA-220 measures oil content on the basis of the conversion to the concentration of "OCB standard solution". "OCB" is the abbreviation of 2,2,4-trimethylpenthane (iso-octane), hexadecane (cetane) and benzene. "OCB standard solution" is a mixture of 37.5 part of iso-octane, 37.5 part of cetane and 25.0 part of benzene.

The unit of measurement is  $\infty$ .Omg OCB/L.

Preparation of span solution generally requires weighing "OCB standard solution" and dissolving it in a prescribed amount of extraction solution (CCL4, for example). OCB mixture is susceptible of evaporation, however, and not easy to be precisely weighed. Besides, a chemical balance may not be available.

Following is a simple preparation process for span solution which does not involve a chemical balance.

## ° Materials required

- ① Carbon tetrachloride or Flon S-316 .... For use in measuring oil content
- (2) 2,2,4-trimethylpenthane (iso-octane))
- (3) Hexadecane (cetane)

Special grade reagents (or their equivalents) (about 100ml each)

- (4) Benzene
- (5) Microsyringe ...... Standard accessory
- 6 1,000ml measuring flask ...... Obtained by customer
- (7) 100ml Erlenmeyer flask with stopper ....
- (8) 10m2 transfer pipet (1 pc.) ......
- (9) 15ml transfer pipet (2 pcs.) ......

[Caution] Avoid prolonged breathing of Flon S-316.

Caution Do not breath carbon tetrachloride fumes.

Do not spill carbon tetrachloride on your skin.

(Note) Clean glass instruments in purified extraction solution (CCL,) and dry them in air before use.

#### Preparation process

1. [OCB standard solution]

Take 15ml of iso-octane, 15ml of cetane and 10ml of benzene in the Erlen-meyer flask by using the transfer pipets, quickly close the flask by stopper, and shake it sufficiently.

The specific gravity of the mixture is 0.769 (20°C).

Caution Do not pipette the halogenated solvents by mouth. Use a pipette bulb!

2. Take OCB standard solution by the amount appropriate to a selected range in the microsyringe and pour it in the measuring flask. Be sure to remove excess solution from the tip of the syringe by filter paper or the like before pouring. Also remove a final drop of solution from the syringe tip by touching the tip to the side of flask after pouring.

	"OCB" Volume		"SPAN" Adjustment Value
20 ppm range	23.0µՁ	17.7 (mgOCB/L)	17.7
5 ppm range	12.0µՁ	9.2 (mgOCB/£)	4.6

- 3. Fill the measuring flask with extraction solution to 1,000ml level, close the flask with stopper and shake it sufficiently. The resultant mixture is span solution.
  - (Note) Use extraction solution for cleaning microsyringes. Be sure to dry the syringes well so that no cleaning solution remains. The concentration may change due to evaporation of the solvent if the flask is left open. Be sure to insert the stopper in the flask when not using the standard solution.
  - \* When B-heavy oil (supplied) is used as calibration oil:
    Usually, measurement unit for sample must be "mgOCB/L".
    Use supplied B-heavy oil, however, when your experiment or study does not require results expressed in "mgOCB/L" (for example, when your experiment is intended for determining the relative value of measurement). If oil subjected to measurement is identifiable, the oil may be used as calibration oil.

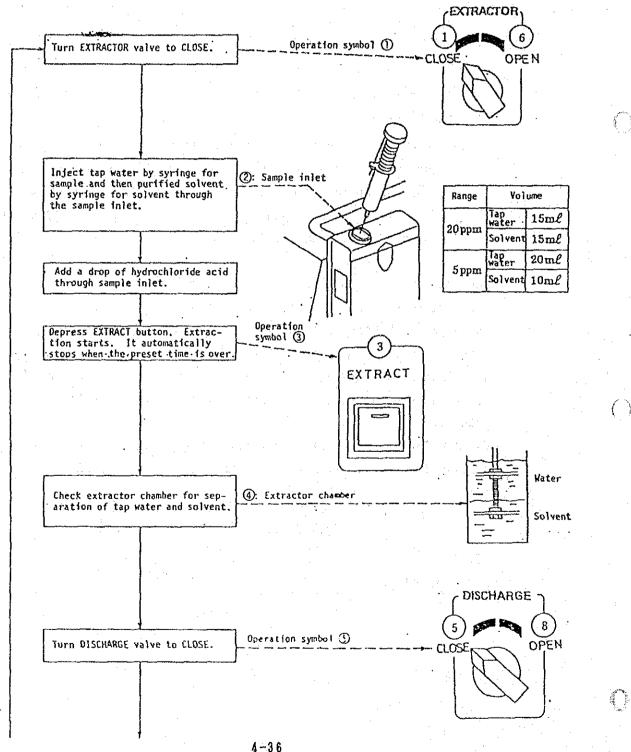
Use 1,000ml measuring flask for preparing span solution. (The preparation process is the same with that for OCB standard solution.)

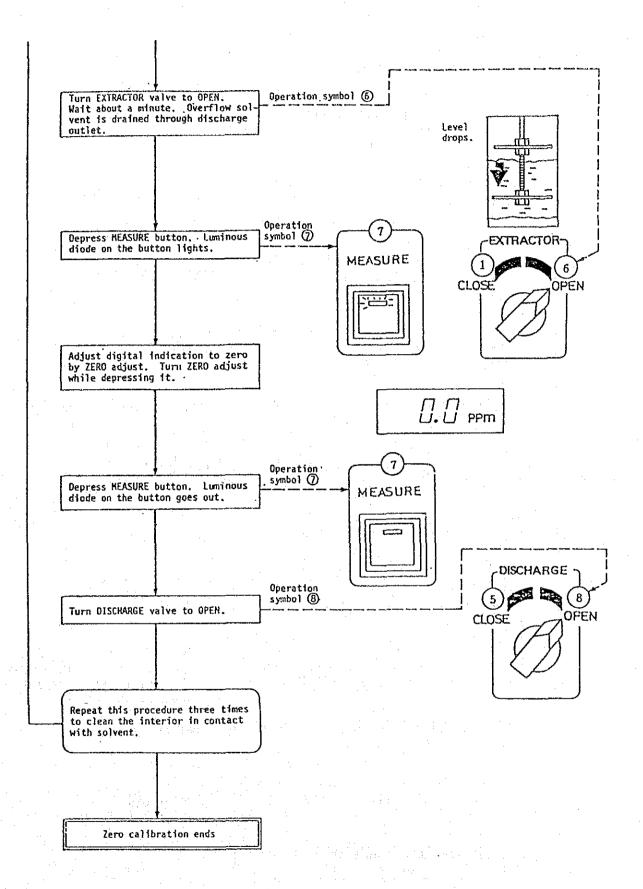
	Volume of B-heavy Oil	Concentration of Span Solution	"SPAN" Adjustment Value
20 ppm range	20.0µՁ	20.0 (µ೭/೭)	20.0
5 ppm range	9.0µՋ	9.0 (µl/l)	4 .5

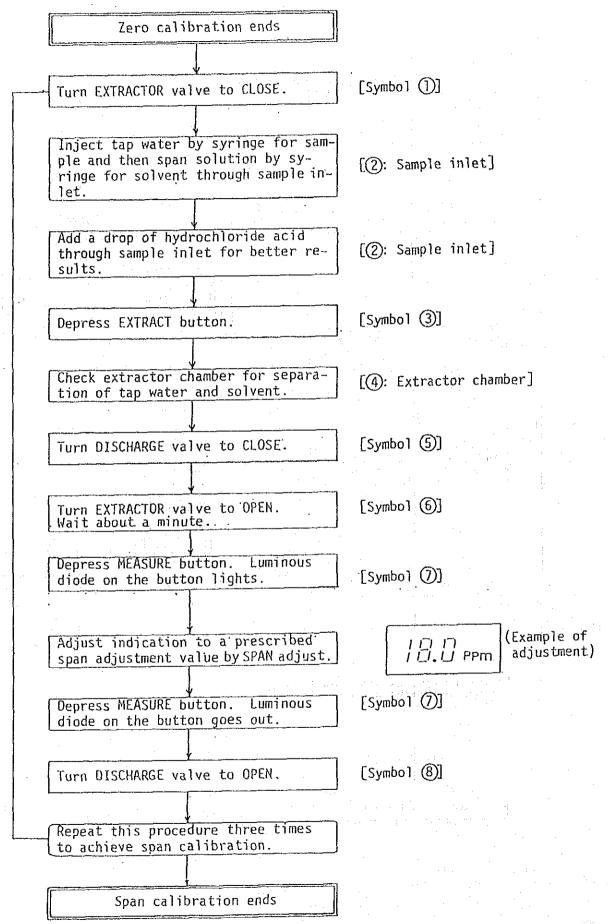
#### 7. Calibration

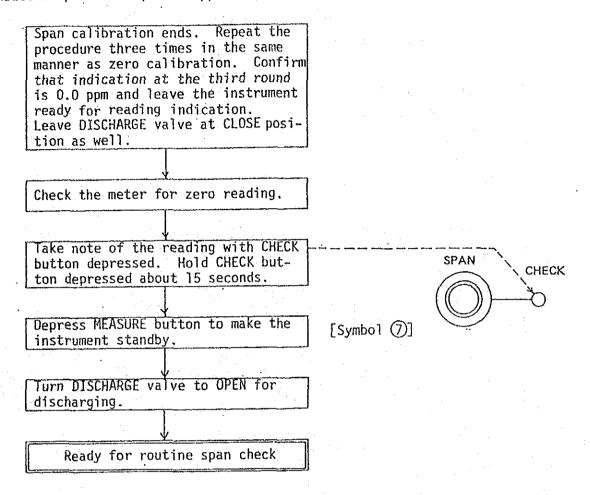
- ° Turn ON the instrument by depressing POWER button on the front panel and wait 30 minutes for warming up.
- ° Depress RANGE to select measuring range.
- ° Set EX.TIME at 40 seconds.
- ° Prepare hydrochloride acid solution (deluted one to one with distilled water).

## .[Zeroing]









Adjust digital display indication to the value taken note of at zero calibration by depressing CHECK button. Then routine span check can be performed without using span solution.

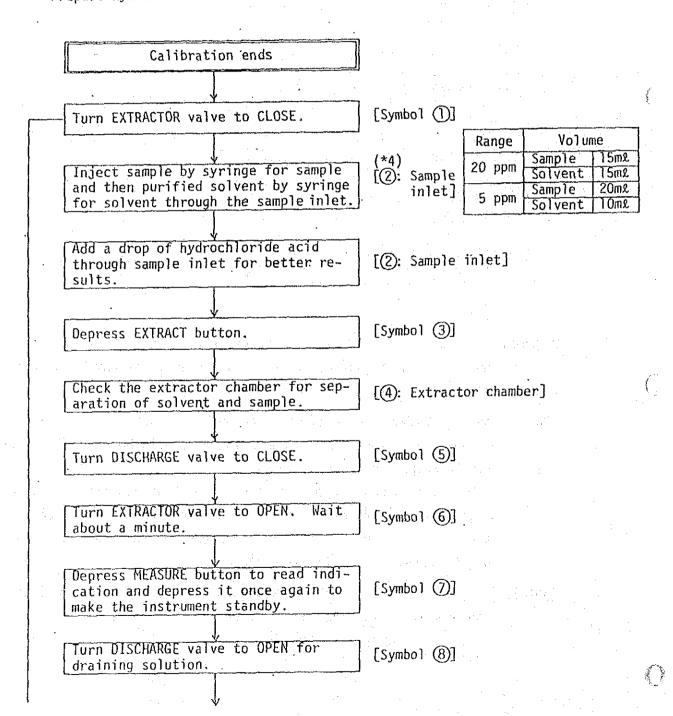
- (Note) The span check by depressing CHECK button is just a simple routine procedure. Calibration by span solution should be primarily relied upon to ensure accurate readings.

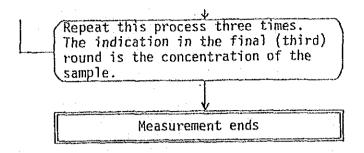
  Do not fail to confirm the reading by CHECK button (routine span checking value) in the procedure shown above whenever calibration by span solution is performed. The frequency of calibration by span solution is once a week in principle.
- (Note) For 5 ppm range, do not depress CHECK button under the above condition; the meter reading would exceed the full scale.

#### 8. Measurement

Instructions are given for use of attached extract first, then procedures for using extractor outside main body.

- 8.1 Measurement by using attached extractor(\*1)
  - ° Select measuring range (\*2).
  - Perform calibrations (zeroing and span calibration) for the selected range.
  - ° Set the extraction time (\*3).
  - Prepare hydrochloride acid solution (deluted one to one with distilled water).





- [Caution] (\*1): The use of attached syringes and extractor may result in inaccurate measurement or cause instrument malfunction if measurement is performed with such sample as described below. It is recommendable, in such a case, to perform external extraction.
  - (1) Sample with oil film or bead on the surface (Syringes cannot be used for taking sample. Total volume of sample water must be used for extraction.)
  - ② Sample containing lots of suspended solids (sand and organic matters)
    - (Such sample, if used, may damage syringes or accelerate clogging in the built-in filter.)
  - ③ Sample containing lots of solvent raising substance (like nonionic surface active agent)
    (Such sample may damage analyzing unit.)

With such sample, solvent layer may remain cloudy after extraction.

- (\*2): The extraction ratio is different between 20 ppm range and 5 ppm range. Therefore, note that it is not possible to read indication for 20 ppm range after extraction is performed for 5 ppm range.
- (\*3): With normal water sample, it takes about 40 seconds to achieve required extraction. To provide for possible variation of the extraction time depending on the water sample state, it is recommendable or preliminarily compare the measurement to that by the external extraction the procedure of which is shown in Paragraph 8.2.
- (\*4): Be sure to rinse the interior of the syringe for sample in purified solvent every time after using it for taking sample. It is recommendable to use the same syringe for sample and solvent addition in that order particularly when sample of high concentration is to be analyzed in 20 ppm range.