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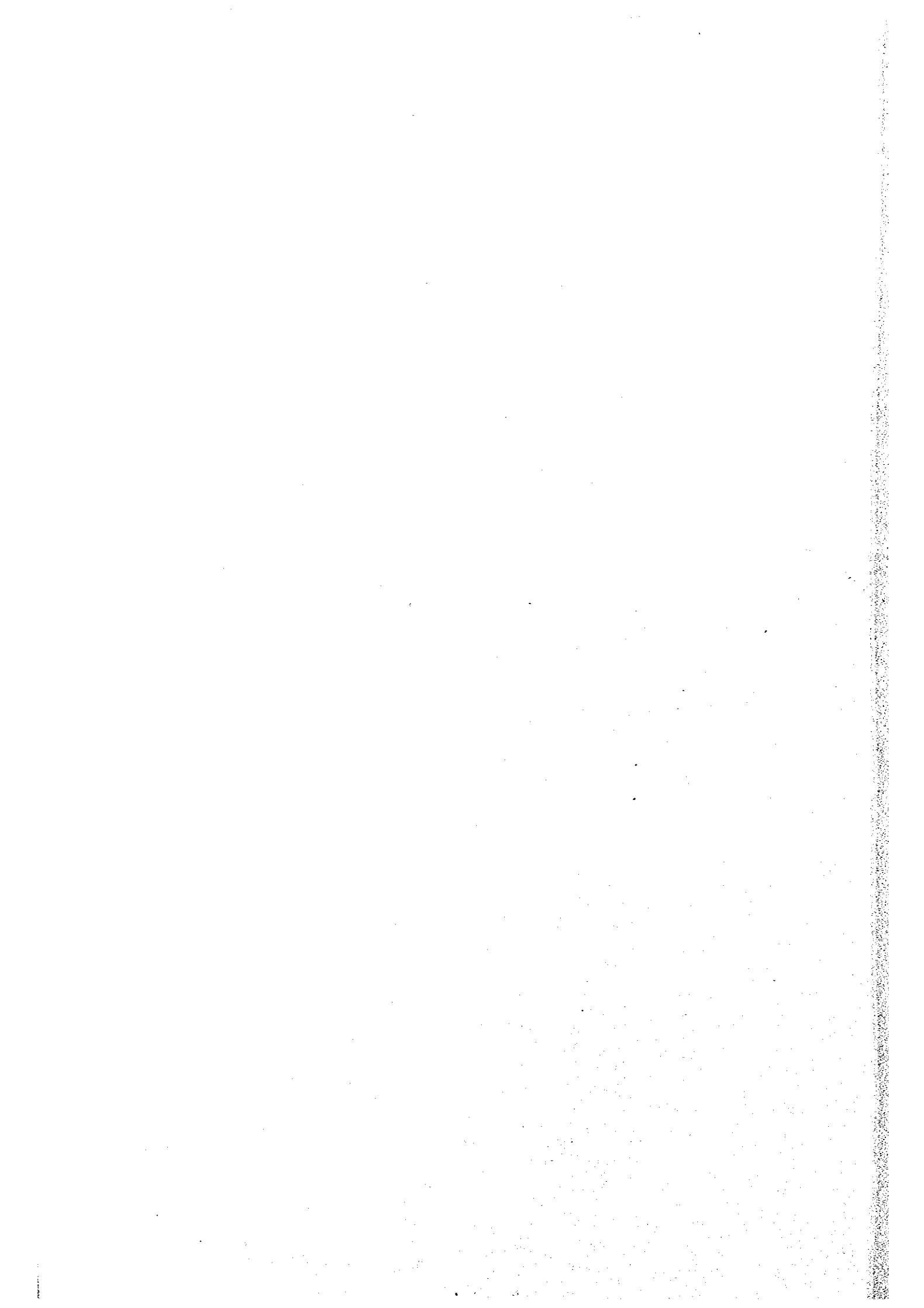
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JAPAN INTERNATIONAL COOPERATION AGENCY  
NATIONAL WATER COMMISSION

**THE STUDY ON  
DEVELOPMENT OF THE NATIONAL WATER QUALITY  
MONITORING PROGRAM IN COASTAL AREAS  
IN THE UNITED MEXICAN STATES**

**FINAL REPORT  
( SUPPORTING REPORT )**

**March 2000**

**PACIFIC CONSULTANTS INTERNATIONAL  
METOCEAN**



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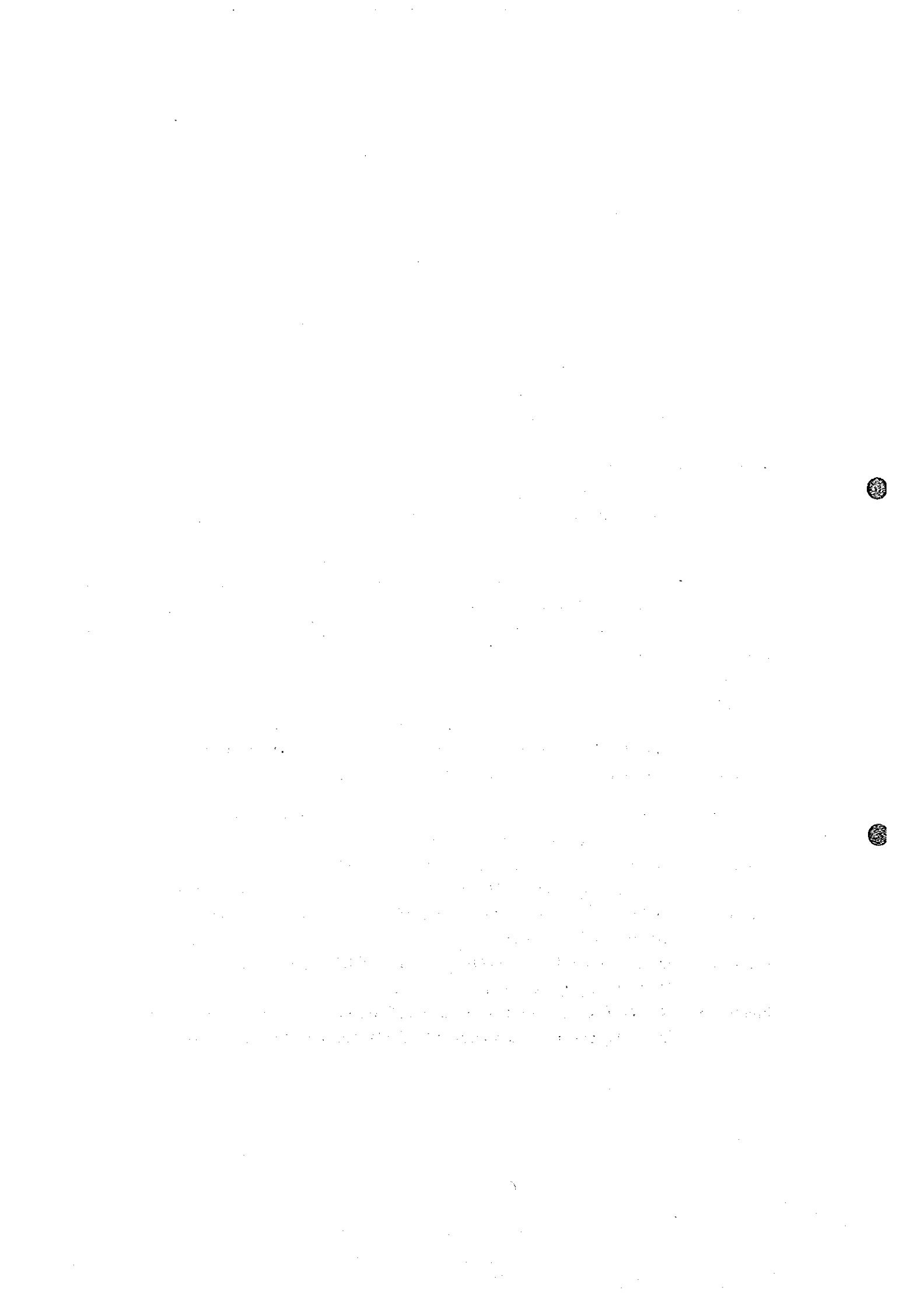
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## Chapter 1 Field Survey Manual for Coastal Water Quality Monitoring

### 1.1 Introduction

Water Quality Monitoring consists of two major components: water sampling and water quality analysis. The subsequent statements best explain the importance of these two components. If samples were to be taken improperly, there would be a great possibility of obtaining incorrect data, even if a precise analysis were carried out. The reverse is also true. An improper analysis would generate incorrect data even if samples were taken correctly. In other words, the water sampling should be handled with extreme care, and the same careful attention should be paid when analyzing them.

Water sampling for Coastal Water Quality Monitoring differs from freshwater monitoring of rivers, lakes, lagoons and groundwater. There are wind waves, swelling, current and changes in tidal level to be considered. Oceanographic phenomena could easily be affected by weather conditions. Heavier equipment is used for Coastal Water Quality Monitoring compared with freshwater monitoring.

This manual explains the sampling method for Coastal Water Quality Monitoring. The Study Team considered that it was more effective to provide know-how on sampling activities based on actual fieldwork rather than theoretical situations.

### 1.2 General Procedure of Monitoring

Monitoring can be divided into three steps: preparatory work, fieldwork and laboratory work, as shown in Figure 1.1.

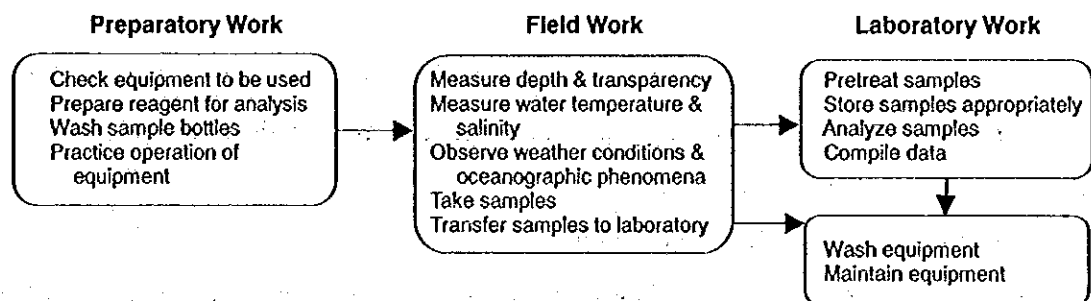


Figure 1.1 Procedure of Water Quality Monitoring

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### 1.2.1 Preparatory Work

It is important that the equipment for sampling and analysis are prepared before any field surveys are conducted. The reagents shall also be prepared and confirmed. Testing of all equipment shall be performed at this stage. A checklist of all activities to be undertaken in the preparatory stage is given below:

- hold a meeting of the Sampling Team and Analysis Team, and define the role of each team member,
- prepare the sampling equipment,
- prepare the analysis equipment and reagent,
- conduct practices on actual operation of equipment, and
- confirm weather conditions.

### 1.2.2 Fieldwork

During field survey, observation of oceanographic phenomena, water sampling and parameter analysis are conducted at monitoring stations. Standard field notes should be used to record all necessary information including location, weather, depth, transparency, sample bottles and others. Samples of field notes are presented in Table 1.1 and Table 1.2.

The following steps shall be followed when undertaking water quality monitoring:

- 1 Obtain present and forecast weather conditions before going on field;
- 2 Bring the equipment and sampling bottles to the survey boat;
- 3 Check the necessary equipment and sampling bottles according to the check list;
- 4 Locate the monitoring station by GPS;
- 5 Anchor the survey boat at the monitoring station;
- 6 Measure the location of monitoring station by GPS;
- 7 Record starting time, weather conditions, oceanographic phenomena, water color, surface water conditions (existence of oil, booming of plankton etc.), observations of surrounding area (passing ship, fishing, construction etc.) on the field note;
- 8 Measure depth and transparency;
- 9 Measure water temperature and salinity;
- 10 Take water samples at 0.5 m below surface (proposed sampling layer) by Van Dorn Water Sampler;
- 11 Take samples for DO analysis, and fix oxygen concentration level;
- 12 Fill up other sample bottles;
- 13 Check the number of sampling bottles;

- 
- 14 Store samples in an ice box;
  - 15 Take water samples at other sampling layers by Van Dorn Water Sampler;
  - 16 Repeat from 14, 15, 16, 17 and 18; then proceed to next step;
  - 17 Measure the location of monitoring stations by GPS;
  - 18 Pull up the anchor;
  - 19 Move to the next monitoring station; then,
  - 20 Repeat from 14.

### 1.2.3 Laboratory Work

Bring everything (sampling equipment and samples) back to the laboratory after completing the survey work. After confirming the number of sample bottles, pre-treat some of the samples, e.g. samples for heavy metals and hexane extract matter. Sample bottles should be stored in an appropriate place, e.g. refrigerator or in a cool dark place, depending on monitoring parameters.

Sampling equipment should be maintained. Some of them, including water sampler, sensors and ropes should be rinsed to eliminate salt.

## 1.3 Preparation of Field Survey

### 1.3.1 Orientation Meeting

During the meeting, the members of the survey team are oriented on the objectives of the survey and scope of work. The duties and responsibilities of each member are also taken up to prevent confusion and any untoward incidents on field. It is very important that necessary information are shared by everyone, and that all is familiar with each other's activities. Specifically, the following topics are discussed.

- purpose of field survey;
- schedule of field survey based on weather conditions;
- location and number of monitoring stations;
- monitoring parameters;
- necessary monitoring equipment; and
- confirmation of each member's activities during the survey.

---

### 1.3.2 Obtain Necessary Information

All necessary information for coastal water quality monitoring that will affect timing and on-field decisions during the survey should be obtained. Such information includes tidal level and weather conditions. Weather stations and experienced boatmen could provide such information to the sampling teams.

### 1.3.3 Check Monitoring Equipment

The team leader should check and confirm the monitoring equipment, such as thermometer, samplers, sample bottles and reagent for pretreatment, based on a prepared checklist (See Table 1.3).

Table 1.1 Example of Field Notes for Water Quality Sampling

Monitoring Area: \_\_\_\_\_ Date: \_\_\_\_\_ Signature \_\_\_\_\_

Monitoring station :		Sampling time : . . . . .			
Weather	Air Temperature .....		Wind Conditions :		
Depth m		Wave Conditions :			
Water color		Transparency m			
Measuring Parameter on boat					
Parameter Equipment Serial No.	W.Temp.( °) STD Serial No.	Salinity STD	pH	DO(mg/l)	
0.5 m	23.1	33.22			
8.5 m	23.3	34.23			
Sampling bottle Check					
Layer (m)	Parameter	Bottle Type	Mark		
0.5	DO	P G 300 ml	✓	<p>Passage ship (11:35)</p> <p>point</p> <p>Red tide</p>	
	SS, COD, T-N, T-P	P G 2 l	✓		
	Coliform	P G 300 ml			
		P G ml			
		P G ml			
		P G ml			
		P G ml			
		P G ml			
		P G ml			
8.5	Cd, Pb, Cu, Zn	P G 2 l	✓	Note :	
	Hg	P G 1 l			
	Pesticides	P G 2 l			
		P G ml			
		P G ml			
		P G ml			

**Table 1.2 Example of Field Notes for Sediment Sampling**

Monitoring Area: \_\_\_\_\_ Date: \_\_\_\_\_ Signature \_\_\_\_\_

Monitoring Station	Sampling Time :    :    •    :	
Weather	Wind Condition	
Depth (m)	Wave Condition	
Sediment Conditions	ORP (mV)	
Particle Condition	:	
Color	:	
Odor	:	
Sampling List		
Parameters	Bottle Type	Mark
Particle size, IL, COD, * *	500 ml Plastic bottle	√
Remark		

Monitoring Area: \_\_\_\_\_ Date: \_\_\_\_\_ Signature \_\_\_\_\_

Monitoring Station	Sampling Time :    :    •    :	
Weather	Wind Condition	
Depth (m)	Wave Condition	
Sediment Conditions	ORP (mV)	
Particle Condition	:	
Color	:	
Odor	:	
Sampling List		
Parameters	Bottle Type	Mark
Particle size, IL, COD, * *	500 ml Plastic bottle	√
Remark		

Table 1.3 (1) Checklist of Monitoring Equipment for Field Survey

Sample Bottle List (Water Sample)

Parameters	Bottle type	Quantity	Check	pretreatment
pH OD SS T-N T-P	2L(P)	62		Cool at <5
c n	300mL(G)	62		In dark place
NH <sub>4</sub> -N O <sub>2</sub> -N NO <sub>3</sub> -N PO <sub>4</sub> -P Chlorophyll-a	2L(P)	62		Cool at <5
			Filtration	
Hexane Extraction(Oil)	2L(G)	24		In dark place
Total coliform Fecal coliform	150mL Bag	36		Cool at < 5°C and In dark place
Cd,Pb,Cu,Zn	2L(P)	21		Include HNO <sub>3</sub>
As	2L(P)	21		Cool at <5
g	1L(G)	21		Include H <sub>2</sub> SO <sub>4</sub>
Aldrin,Dieldrin, Endrin,DDT,Chlordane				Cool at <5 In dark place

Notes (P) means plastic bottle and (G) means glass Bottle.

Sample Bottle List (Bottom Sediment)

Item	Bottle type	Quantity	Check	pretreatment
Sediment Basic items Inorganic matters	1L(P)	21		Cool at <5

Table 1.3(2) Checklist of Monitoring Equipment for Field Survey

Date

Name of equipment	Quantity	Initial Check	Final check	Notice
<b>For Water Sampling</b>				
GPS		Data input Battery		
Field Report				
Compass				
Forel Color Indicator				
Depth Meter				
Secchi Disc				
STD		Charger Battery Chart paper Sensor Code Rope Motion Check		
pH Meter		Battery Standard Motion Check		
3L Bandon Water Sampler		Spare parts Rope		
6L Bandon Water Sampler		Spare parts Rope		
Plastic Funnel				
Iced Box				
Sampling Bottles				See accompanying paper
<b>For Sediment Sampling</b>				
Field Report				
ORP Meter		Battery Motion Check		
Thermometer				
Ekman-Berge Sediment Sampler		Spare parts Rope		
Smith-McIntyre Sediment Sampler		Spare parts Rope		
Tub				
Scoop				
Ice Box				
Sampling Bottles				See accompanying paper
<b>Others</b>				
Life Jackets				
Chart Map				
Stationery				
Others				

Signature



## 1.4 Navigation

### 1.4.1 Basic Principle of GPS

Global Positioning System (GPS) is a very convenient tool for navigation, positioning, time dissemination and other research. The use of GPS is recommended for navigation of monitoring boats.

The GPS constellation consists of 24 satellites (called space vehicles or SVs) that orbit the earth. A GPS receiver processes specially-coded satellite signals to compute position, time and velocity. There are hand-held models and those installed onboard vehicles or fitted on any object that needs to be monitored. Figure 1.2 pictures the principle of the GPS system.

However, the accuracy of GPS is dependent on the satellites, which are controlled by the U.S. Department of Defense (DOD). In fact, the DOD degraded the accuracy of satellite signals at the outbreak of the Gulf War. The potential accuracy of around 20 to 30 m is sometimes reduced to 100 m. But aided by an electric power bureau on land, the accuracy of GPS can be enhanced.

The GPS is not only used in aircraft and ships. In recent years, surveyors, hunters, hikers and dispatchers, who route delivery vans and emergency vehicles, have used GPS. Also, automobile manufacturers are offering moving map displays guided by GPS receivers.

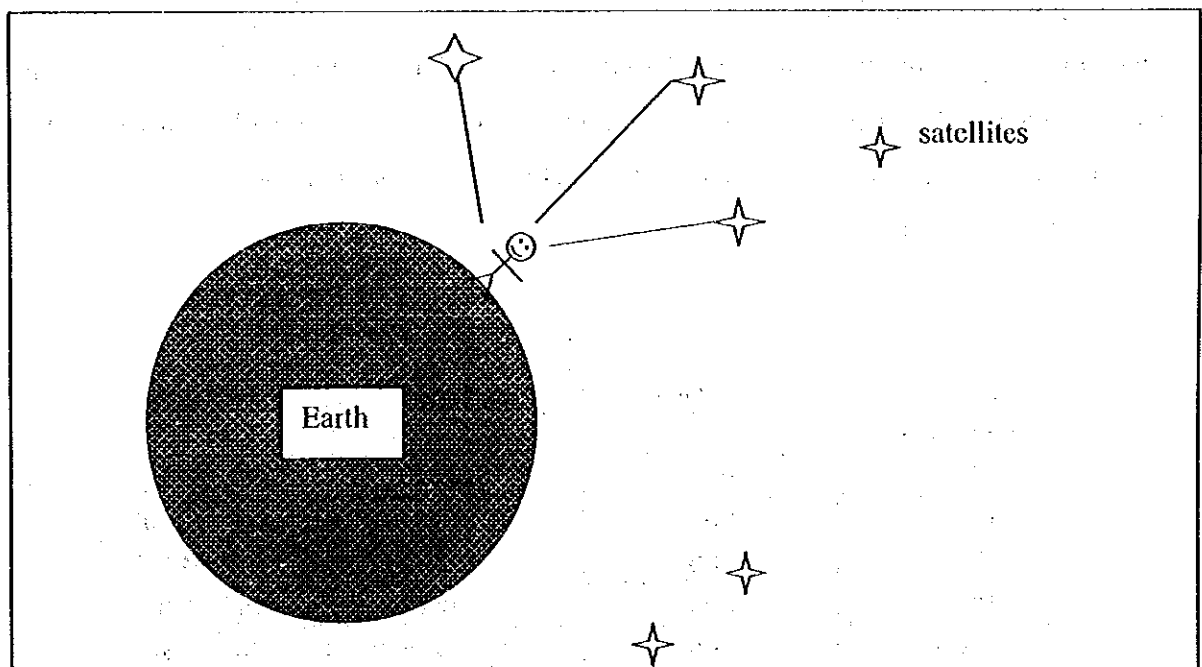


Figure 1.2 Principle of GPS System

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## 1.4.2 Preparation for Using GPS

Before using the GPS, there are two things that need to be done first:

- initializing, and
- data input.

### (1) Initializing

As mentioned earlier, a GPS receiver processes signals coming from SVs. Approximate orbital data parameters for all SVs are called almanac. Signal acquisition on receiver startup can be significantly aided by the availability of current almanacs. The approximate orbital data is used to preset the receiver with the approximate position and carrier Doppler frequency (the frequency shift caused by the rate of change in range to the moving SV) of each SV in the GPS constellation.

In order to get a good microwave signal, it is necessary to input the user's present position and time. This procedure is called "initialization." Time is entered either in local time or Greenwich Mean Time. There is no need to initialize the GPS receiver again as long as the user keeps within a radius of 450 km from present position. But if the user moves to another position over 450 km away, the GPS has to be initialized again.

### (2) Input Location Data

Although it is possible to begin using the GPS after the initialization process, by inputting positional data, called "landmark," its use becomes much easier. "Landmark" consists of data on longitude and latitude, altitude and position. However, before inputting these data, a list, as shown below, should be prepared.

Table 1.4 Location Data

Station	GPS Name	Latitude	Longitude
<b>Panuco River</b>			
PR-1	PR1	22° 15.20'	97° 48.36'
PR-2	PR2	22° 14.15'	97° 49.90'
PR-3	PR3	22° 12.40'	97° 51.08'
PR-4	PR4	22° 13.61'	97° 53.84'
PR-5	PR5	22° 13.35'	97° 53.98'

---

### 1.4.3 Navigation by GPS

There are certain things to remember when using the GPS. They are briefly discussed below:

#### (1) Use of Batteries

The batteries in GPS receiver models usually last almost 20 hours. The important point to remember is that if the GPS is without batteries for more than 20 minutes, all almanac data and landmark data contained in the GPS receiver would be completely lost.

#### (2) Time to Turn on the Receiver

It is better to turn on the GPS receiver before the start of the survey because it usually takes sometime for the receiver to get a signal from the satellites.

#### (3) Selection of Next Point

The landmark of next point can be set with the "Go To" key, which can set the GPS screen to any of the following options: Position Screen, NAV screen, Pointer Screen, Plotter Screen and so on. The Position Screen, NAV Screen and Plotter Screen are often used basically.

##### a) Position screen

This is the most basic screen. It shows the user's present position (latitude and longitude), elevation, time and date

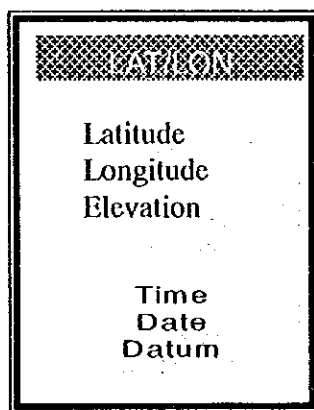


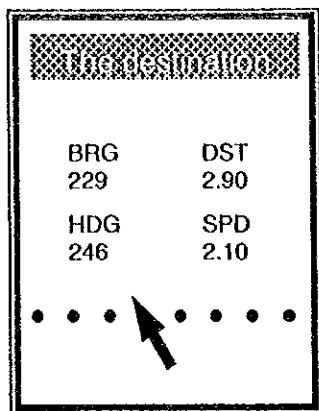
Figure 1.3 Position Screen Display

##### b) NAV screen

This screen shows data of the destination. It indicates the next position on the upper part of the screen.

The following information is shown in the middle part:

- BRG : Bearing to destination
- DST : Distance to destination
- HDG : Heading
- SPD : Speed



The arrow at the bottom part of the screen is called "CDI" or *Course Deviation Indicator*. The CDI gives the user's present position relative to the planned course, giving an indication of how far left or right the boat is from the planned course and the directional turn needed to get back on course.

Figure 1.4 NAV Screen Display

c) Plotter screen

This screen keeps a historical record of the route traveled, plus the bearing and distance to the destination, which are indicated at the top of the screen, as shown in Figure 1.5.

The next position appears on the upper part of the screen. The arrow represents present position, the flag mark is the destination, and the straight line indicates the plotted course line. The plotter scale is shown in the lower portion of the screen, and can be adjusted from 0.20 to 100 miles. The selected scale represents the distance from the left to the right edge of the screen.

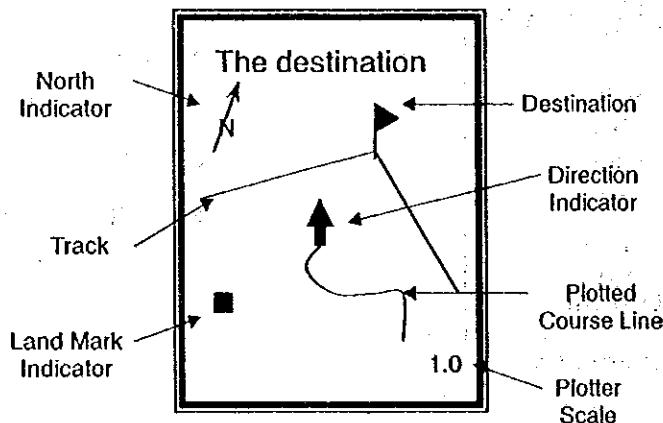


Figure 1.5 Plotter Screen Display

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#### (4) How to Navigate

As mentioned earlier, the GPS should be turned on before leaving port. The known point should be measured and compared with the GPS data. Positioning should be done as follows:

- reduce the speed to 0.1 miles on nearing the monitoring station;
- stop at 0.05 miles from the monitoring station, and approach the monitoring station by inertia; and
- bring the boat to anchor after measuring the distance to the monitoring station.

### 1.5 Water Quality

#### 1.5.1 Necessary Equipment

There are several water samplers; so the most appropriate one should be selected based on sampling purposes, water area conditions, parameters to be analyzed and others. Some of the water samplers and equipment for water quality survey are shown in Figure 1.6. A Van Dorn water sampler is commonly used for coastal water quality monitoring because a large volume of samples can be taken at specific layers.

Water buckets can also be used for sampling of surface water. However, it is difficult to have uniformity of samples because of floating matters distributed on the surface. But the use of water buckets is the simplest method for water sampling and if they were to be used, they should be clean and preferably made of plastic. Buckets for sediment sampling or plankton sampling should not be used for water sampling.

#### 1.5.2 Water Sampling

Aside from utilizing an appropriate sampling method, the following should be considered in water sampling for water quality monitoring:

- sampling period,
- monitoring stations,
- sampling layer,
- analysis parameters, and
- sampling frequency (high tide, low tide and so on).

Water depth and transparency should be measured for water quality monitoring, while oceanographic phenomena should be observed.

Water sampling is to be done as quickly as possible if the surveyor is on a boat. Furthermore, the following points should be carefully considered:

- 1 Water samples should be taken at the front or side of the boat where there is less

---

possibility of wastewater contamination by oil leakage from the boat's engine, mixture of foreign substances and others.

- 2 Water sampling bottles should be separated from plankton sample bottles to avoid contamination. Formalin, acid and alkaline should be kept away from other sampling bottles.
- 3 Water buckets and bottles for sampling should be washed, at least twice, using water from where the water samples would be taken. Sampling funnels should also be washed. When using the funnel, be careful not to get the dripping water from the sample bottle into the sample bucket. Plastic bottles shall be fully filled, while glass bottles shall be filled up to the shoulder level of the bottles.
- 4 Though it is desirable that water samples be directly transferred from the sampler to the bottle, a clean plastic bucket could be used. Water buckets used for water sampling should not be used for sediment and biological sampling and any other purposes.
- 5 When filling up the sample bottles, there should be a uniform amount of water taken.

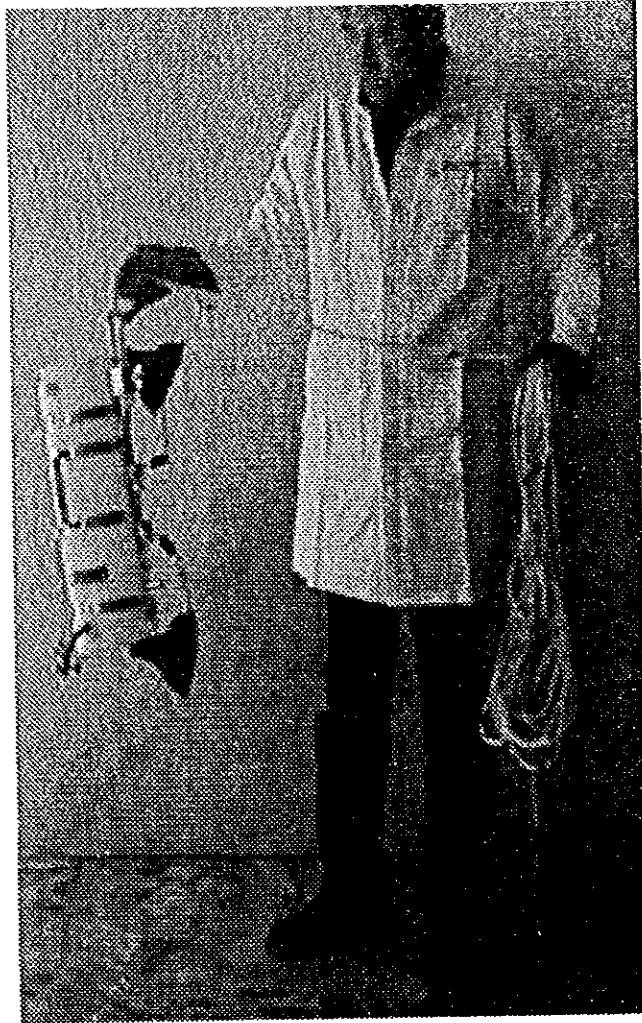


Figure 1.6 (1) Photograph of Sampling Equipment

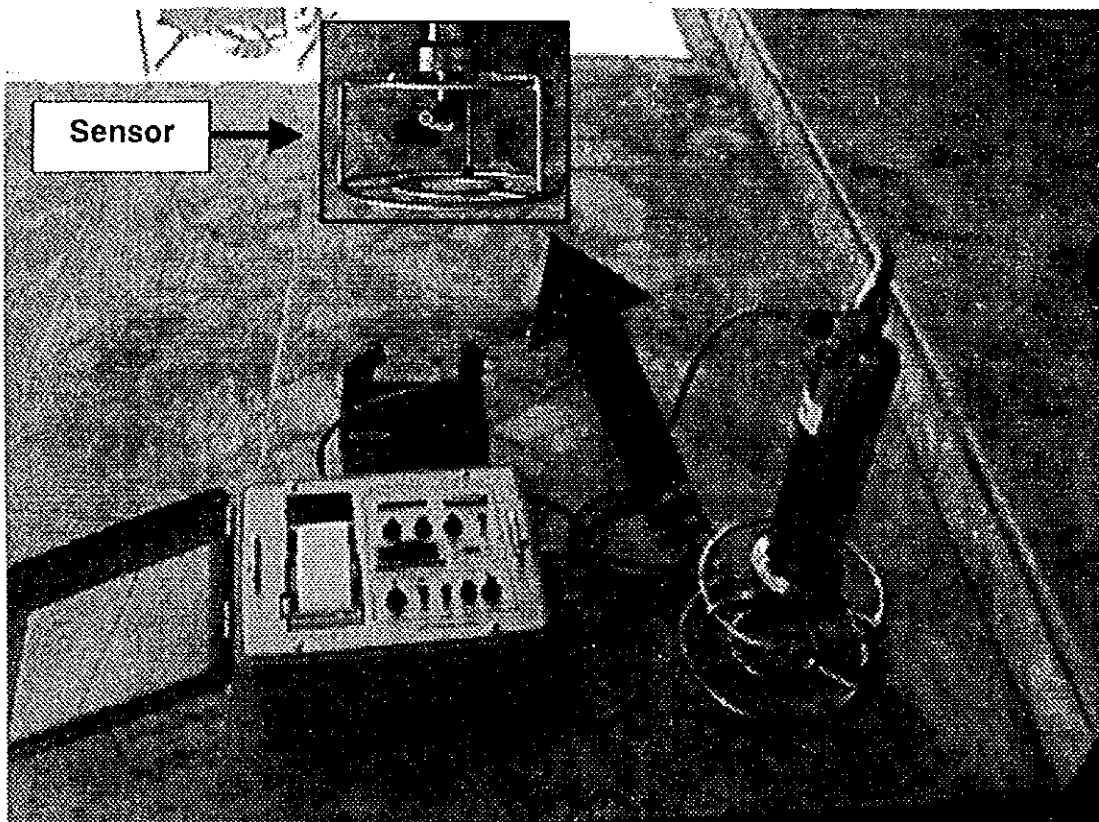
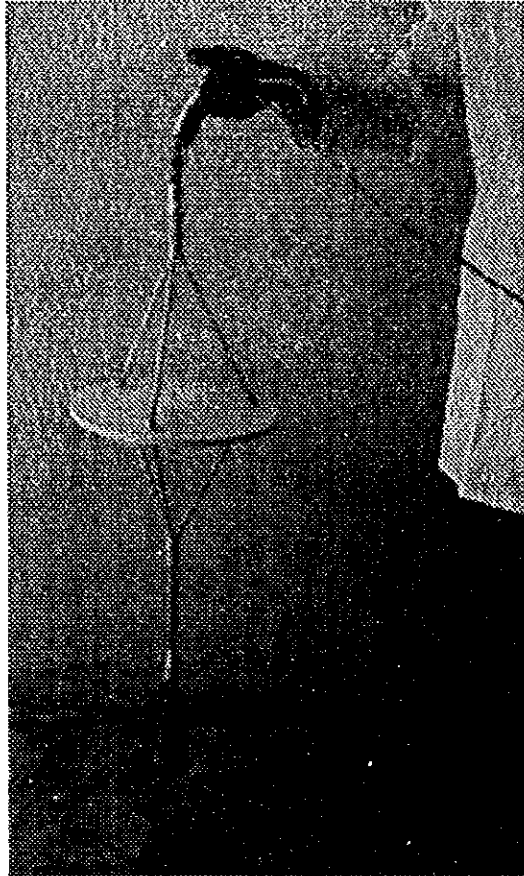


Figure 1.6 (2) Photograph of Secchi Disc and STD System



- 
- (1) Depth
    - a) Record the depth straight away. If there are currents, drop a sounding lead of measure in the upstream. ---See Figure 1.7.
    - b) When the sounding lead lands at the bottom, pull it up a little and then drop it again. Do this several times for confirmation of depth.

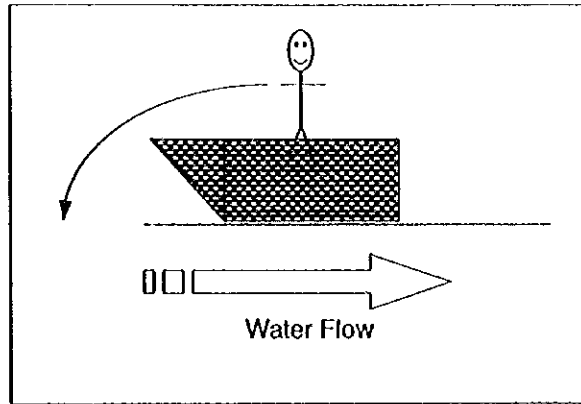


Figure 1.7 Direction where the Anchor is Dropped

- (2) Transparency
  - a) Measure the transparency of water with your back to the sun
  - b) Lower the Secchi disc into the water
  - c) Measure the distance when the rope between the Secchi disc is visible and when it is no longer visible.
  - d) Take care that the Secchi disc does not go under the boat
- (3) Water Color
  - a) Measure the color of water with your back to the sun
  - b) Observe which surface does not reflect sunlight
- (4) Wind Condition
  - a) Determine wind direction by observation, e.g. direction of smoke,
  - b) Determine wind conditions by observation, as indicated in Table 1.6
- (5) Wind Wave
  - a) Determine current direction by observation, e.g. direction of drifting matter like driftwood
  - b) Determine wind wave conditions by observation, as indicated in Table 1.5.
- (6) Measure the temperature and salinity of water by STD

- 
- a) 10 seconds after turning the STD instrument on, it will begin measuring. Lower the STD sensor to just under the surface of the water after suspending it on air for 5 minutes
  - b) After 5 seconds, lower the STD sensor to below 0.5m/sec;
  - c) When the sensor lands at the bottom, pull it up quickly
  - d) Wipe the connectors all around
  - e) Plug in the connector and lock it
  - f) Turn on the printer
  - g) Confirm the printed data
  - h) The following error messages may appear:
    - “MISMATCH” : This message may be attributed to the following:
      - The connectors may still be wet. Wipe the connectors, reset and turn it on once again.
      - The battery is low. Change the battery.
 Unusual data is printed out (e.g. water temperature is 80°C, salinity is a minus number).
      - This is caused by motion error. Reset and turn on again.
 “DATA EMPTY”: If this message appears after checking the above, repeat the measurement.
  - i) After confirming that the data does not have any error, turn the STD off.

Table 1.5 Table Beaufort Wind Scale

Class	Explanation	Height of waves
0	Surface is like a mirror.	0
1	There are ripples.	0 to 0.1
2	Wave crest is glassy.	0.1 to 0.5
3	Little waves.	0.5 to 1.25
4	Pretty waves.	1.25 to 2.5
5	Waves are more or less high.	2/5 to 4/0
6	Waves are very high.	4.0 to 6.0
7	Waves are rough.	6.0 to 9.0
8	Waves are quite rough.	9.0 to 14.0
9	Abnormal.	Over 14.0

**Table 1.6 Classification of Wind Waves**

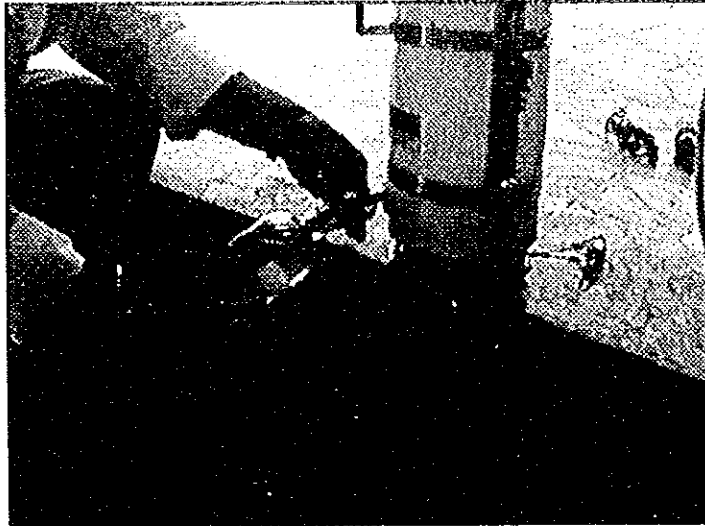
Class	Wind velocity		Explanation	
	m/s	km/h	On the land	On the ocean
0	0.0 to 0.3	Under 1	Smoke rises straight above.	Surface is like a mirror.
1	0.3 to 1.6	1 to 6	Direction can be determined but not felt.	Ripples are like scales.
2	1.6 to 3.4	6 to 12	Wind can be felt. Leaves are moving.	Short waves are seen clearly. The top of waves is glassy.
3	3.4 to 5.5	12 to 20	Leaves and twigs are constantly moving.	The top of waves begins to break. Sometimes white-crested waves appear.
4	5.5 to 8.0	20 to 29	A cloud of dust rises. There are pieces of paper flying.	There is an increase of white-crested waves.
5	8.0 to 10.8	29 to 30	Shrubs begin to swing. A wave crest appears on the lake and pond.	A lot of white-crested waves appear; a spray sometimes appears.
6	10.8 to 13.9	30 to 50	Big branches are swaying. It is difficult to use an umbrella.	Big waves are formed.
7	13.9 to 17.2	50 to 62	Trees are swaying. It is difficult to walk against the wind.	Waves become bigger. White bubbles begin to appear everywhere on top of the wave.

**(7) Water Sampling**

Observe the condition of the survey area during water sampling. For example, do not take a sample on current rips because that is an abnormal condition. Should another boat pass near the survey boat, wait a few minutes before taking any samples to allow the bottom sediment to settle.

Use a small sampler (3L of Van Dorn water sampler) for DO, VOC, and coliform sampling, and a big sampler (6L of Van Dorn water sampler) for other parameters. If only one water sampler could be used, start with DO and VOC sampling.

- a) Set the water sampler, but avoid touching the area between sampler and cap.
- b) Lower the sampler to the desired depth. If the sampler could not be properly positioned because of the stream, use a weight. Slowly lower the sampler to the bottom, measure the rope length, then pull it up to the desired depth.
- c) The water sampler should be pulled up and down in the sampling layer in order to eliminate air from the sampler.
- d) Pull up the water sampler and open the upper cap to allow the air to escape.
- e) Open the sampling cock, then wash the tube. Turn up the mouth of the tube to push out the air.



f) Take water samples for DO analysis, followed by VOC, then coliform.

g) For DO sampling

- 1 Lower the sampler to the desired depth. Move the sampler up and down at the sampling layer in order to eliminate the air from the sampler. Then drop a messenger and slowly pull up the sampler.
- 2 Insert the tube of the sampler in a DO sampling bottle and fill it with water sample. While doing this, be careful that bubbles are not formed. Also, keep the mouth of the tube under the surface of the water sample, as shown in Figure 1.8.
- 3 Allow the water to overflow to about twice the volume capacity of the bottle to rinse the bottle.
- 4 When the bottle is full, pull the tube from the bottle slowly.
- 5 Carefully add the fixed solution into the DO bottle using a komagome pipette.
- 6 Close the cap and turn the sampling bottle upside down to confirm that there are no bubbles. (If bubbles appear, repeat the sampling.)
- 7 Shake the bottle about 30 times.

h) For VOC sampling

The sampling method of VOC is basically the same as DO sampling.

- 1 Put the tube into the VOC bottle and fill it with water sample. While doing this, be careful that bubbles are not formed. Also, keep the mouth of the tube under the surface of the water.
- 2 Overflow the water samples about twice the bottle's capacity to rinse the bottle.
- 3 When the bottle is full, pull the sampling tube from the bottle slowly.

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4 Put a little water in the cap and screw the cap on carefully, taking care that bubbles are not formed.

i) For coliform sampling

- 1 Do not touch the mouth of the sampling tube and the mouth of the sampling bag.
- 2 It is not necessary to rinse the bottle with water from the sampling area.
- 3 Use two sampling bags.

ii) For Hexane Extracts

Do not touch the inside of glass bottles and caps to be used for sampling of n-hexane extracts, i.e. oil and grease, after they have been washing. The following may be used for sampling:

- special sampler for hexane extracts; or
- normal water sampler (water sample is poured into glass bottles).

From the viewpoint of contamination, the first method is better than the second one. However, care should be taken that only surface water is collected. In the second method, it would be better to limit the times that water samples are transferred because the surface of the sampler or bucket may absorb the oil and grease.

### 1.5.3 Sample Bottles

Water samples are ordinarily preserved in clean appropriate plastic or glass bottles with a tight stopper in order to prevent outside contamination. It is very important that careful attention is paid to prevent any mistake in terms of type of bottle used, volume of water sample, and washing method, since the parameters to be analyzed could be affected by these items.

The sample bottles should be labeled appropriately. It should indicate the date, code number of monitoring station and analysis parameter. Figure 1.9 is a sample of a label used in the pilot monitoring survey in Tampico.

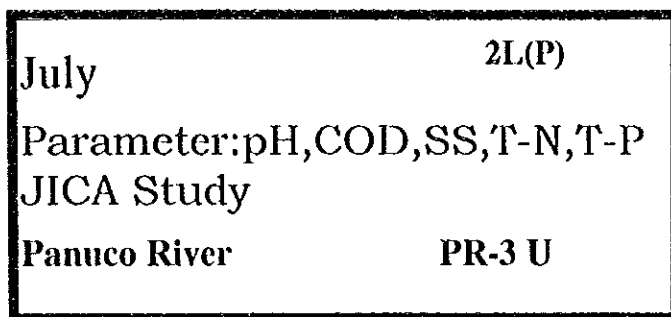


Figure 1.9 Example of a Bottle Label

### (1) Types of Sample Bottles

Sampling bottles are made of either glass or plastic; each one has different features. The choice of which type to use depends on the monitoring parameters.

#### a) Plastic Bottles

The most frequently used type of sample container is plastic bottles, which are handy and can withstand strong impacts and harsh chemicals. In general, there is little elution from plastic bottles; however, Mo, Cr, Ti and others are eluted from some products.

Plastic bottles have a tendency to absorb phosphorus and other organic compounds. Since polyethylene bottles are porous, this can cause water to evaporate, turn water samples into concentrated mixtures and promote the production of algae.

#### b) Colorless Borosilicate Glass Bottles

It is easier to observe samples when stored in a glass bottle. Furthermore, the rate of deterioration of water samples is relatively small in a colorless borosilicate glass bottle. However, borosilicate glass bottles are fragile; its constituents (Si, Na, K, B, Al and so on) are eluted. As, Sb, Zn and so on are also eluted from some products. For analysis of silicates, plastic bottles are more appropriate than glass bottles.

### (2) Washing of Containers

In general, containers are washed with acids, detergents, or cleansers. Containers are rinsed with water frequently enough to eliminate alkali, oil and grease, surfactants and so on. After a thorough washing, a special washing for analyses of metal, coliform, hexane extracts and so on is carried out. For example, sample bottles for analysis of coliform are sterilized under pressurized and heated condition after a thorough washing. Sampling bottles for analysis of

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n-hexane extracts are washed with n-hexane several times. After washing, the inside of bottles and lids should not be touched wherever practicable.

#### 1.5.4 Pre-treatment

Water samples should be analyzed immediately after sampling. It is necessary to pretreat some samples because suspended materials, phenols, cyanides and others are easily transformed with the passage of time (see Table 1.7).

#### 1.5.5 Transportation

It is necessary to recheck all water and sediment samples. It is also necessary to check whether some samples require pretreatment.

#### 1.5.6 Storage of Samples

At the time of preservation and transportation of samples, it is very important to be constantly aware of any condition that may change the nature and constituency of the samples. The samples should be refrigerated or frozen after pretreatment (fixation), if necessary. Leakage of samples and breakdown of containers should be avoided.

While still in the boat, the samples should be protected against direct sunlight and rainwater; they should be preserved in a dark, cool place, such as an icebox, wherever practicable. Water samples should always be preserved separately from biological samples, even during transportation of the samples to the laboratory.

### 1.6 Sediments

#### 1.6.1 Necessary Equipment

There are several types of sediment samplers as follows:

- dredge type sampler,
- glove type sampler, and
- core sampler.

It is possible to conduct sediment sampling while in a boat by using a sediment sampler. Each one of the above mentioned sediment samplers has its own merits. A dredge type sampler (bucket type) could cover a wide area; however, it can cause the diffusion of small sediment particles on the seabed while being pulled by a boat.

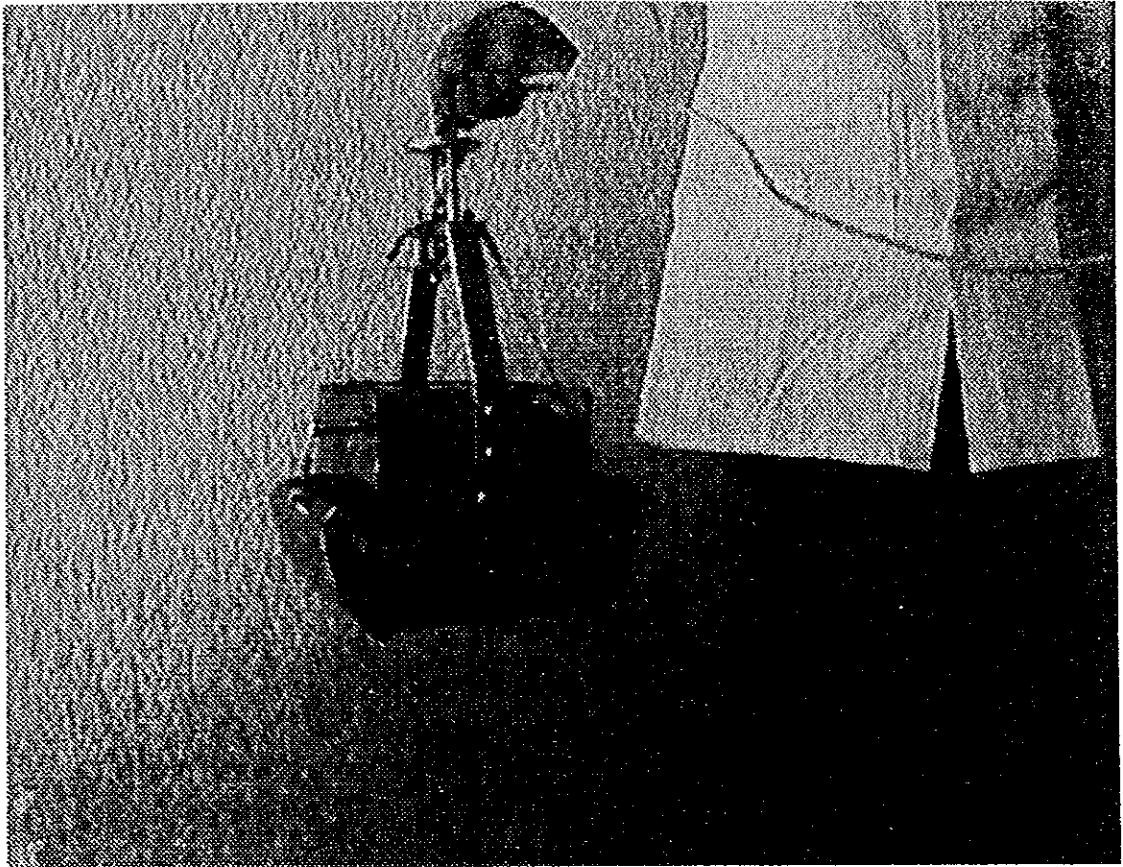
Both the glove type sampler and core sampler are categorized as point samplers. Some glove

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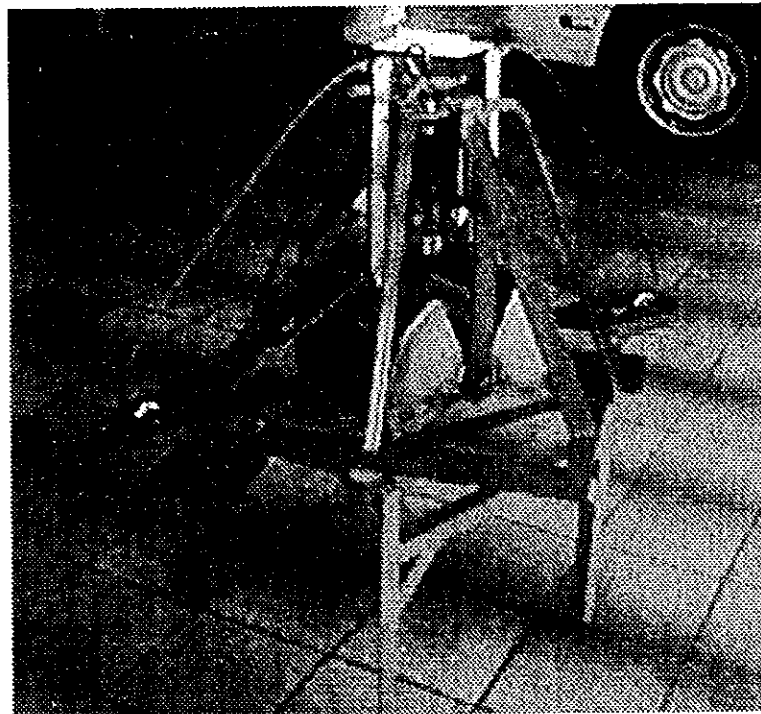
type samplers are the Smith-McIntyre and Ekman-Berge, which are shown in Figure 1.10. They can take top sediment samples 4 to 8 cm deep depending on sediment conditions. They can also take samples from fix sections to be used for quantitative sampling such as benthos survey.

The Smith-McIntyre and Ekman-Berge Sediment Samplers can be used under different sediment conditions; the former, for sand sediment and the latter, for mud and silt sediment. It is better to use a core sampler when identifying a sediment layer. A sediment sampler should not be used when oil or grease is present.





Ekman-Berge Sampler



Smith-McIntyre Sampler

Figure 1.10 Photograph of Sediment Samplers

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### 1.6.2 Sediment Sampling

Unlike sampling on land, sediment sampling at sea is more difficult because sea bottom conditions cannot be directly observed, plus there is the influence of water currents.

Sediment sampling is conducted in the following manner: A boat is anchored in a monitoring station, and sediment samples are taken at least 3 times using an appropriate sampler. The samples obtained in the above process are homogeneously mixed in a bucket or tray and then transferred to a sampling bottle and plastic bags. Buckets or trays, which are used for biological analysis, are put in a fishing boat; metallic materials should not be used for sediment sampling. The Ekman-Berge Sediment Sampler is small and easy to use. However, it is better to use a Smith-McIntyre when taking samples from sandy sea bottom. The procedure of sediment sampling by Ekman-Berge is as follows:

- a) Set the sediment sampler; be careful not to pinch your fingers
- b) Take it down until it is about 1 to 2 m from the bottom of the sea
- c) Wait until the sampler is in upright position
- d) Then drop it to the bottom of the sea
- e) Drop a messenger to close its mouth. Remember to keep the sampler straight
- f) Afterwards, pull up the sampler slowly to confirm that it dug into the bottom sediment, then pull it all the way up to the boat
- g) Put the sediment samples in a plastic bucket or tray
- h) Record the condition of the samples as to type of sediment (silty, sandy, etc), color, odor, with oxidizing zone or not, sediment temperature, and others
- i) Measure ORP
- j) Mix the samples
- k) Put the samples in a sample bottle uniformly; be careful not to leave any aperture to prevent oxidation of samples

### 1.6.3 Sample Containers

Polyethylene bottles of 500-ml. capacity are ordinarily used as sample containers. Clean plastic bags could also be used as sample containers. New bottles, washed with acid and then thoroughly rinsed with water, should be used as sample containers of general items, items relating to harmful substances, and elution examination, excluding those for analyses of particle size, specific gravity, and ignition loss.

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Samples are usually taken in the following manner:

- For basic parameters (e.g. particle size, ignition loss, COD), and inorganic matter (e.g. heavy metals), use plastic bottles
- For sulfide (it is necessary to fix the reagents on boat), use plastic bottles
- For organic compounds (e.g. pesticides, PCB, VOC), use glass bottles

#### 1.6.4 Storage of Samples

Though samples for analysis of particle size and specific gravity may be preserved at room or outdoor temperature, some precautionary measures should be undertaken in the preservation and transportation of samples for analysis of basic parameters and harmful substances, to wit:

- Keep the samples in an icebox, if possible, while in the boat, or in a dark, cool place, wherever applicable;
- The samples are to be preserved in an icebox during transportation;
- Sediment sample bottles should be separated from biological samples, such as water samples; and

### 1.7 Biological Survey

#### 1.7.1 Types of Plankton Sampling

Plankton is a general term to define the organisms floating under water with little or no autokinetic energy. It includes hundreds of different species of zooplankton and phytoplankton, of which morphology and size varies from microscopic level to some meters. Therefore, the selected method of plankton sampling should address a study's objectives.

Plankton sampling can be carried out in two ways: one is by using a water sampler, the other is by plankton net. The difference between the two methods is presented in the table below:

Table 1.7 Method of Plankton Survey

Instrument	Advantages	Disadvantages
Water Sampler	<ul style="list-style-type: none"><li>• handy</li><li>• possible to take microplankton to nano picoplankton</li></ul>	<ul style="list-style-type: none"><li>• difficult to take large volume of sample (about 1 to 5 l)</li></ul>
Net	<ul style="list-style-type: none"><li>• possible to take a large volume of samples</li></ul>	<ul style="list-style-type: none"><li>• easy to be stopped</li><li>• when a net with large mesh is used, small plankton can slip through the mesh</li></ul>

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### (1) Water Bottle Sampling

This method utilizes a water sampler (e.g. Van Dorn water sampler) or pump to take a certain amount of seawater, and then concentrates the samples either by centrifugation or sedimentation method.

Samples taken by this method, like the phyto- and zooplankton, and other larger organisms, are usually for observation. The Tokyo Metropolitan Government, for example, uses a combination of water bottle sampling and sedimentation for the monitoring of both phyto- and zooplankton.

### (2) Plankton Net Sampling

By contrast to the water bottle method, samples taken by plankton nets are for the investigation of larger kinds of phyto- and zooplankton. However, at present, net sampling is hardly practiced for phytoplankton survey in coastal waters. The disadvantage of net sampling is that smaller-scale organisms slip through large net mesh. However, if the mesh is too fine, clogging becomes a major problem. The size and shape of plankton nets vary as shown below. A net basically consists of three components: the top, filter tube, and the bucket (Eimer).

The KITAHARA type net and NORPAC net (North Pacific Standard Net) are generally used. These nets have a common point size of NXX13 (0.1 mm) and NGG54 (0.3 mm). The NORPAC net is the most famous type; however, it is not suitable for environmental survey by small boat because of its large body. The KITAHARA net is comparatively smaller, and more suitable for survey by small boat. In addition, it has a smaller point. So the KITAHARA net is advisable for survey use in the coastal areas where many small zooplankton exist. A drawing of the KITAHARA net is shown in Figure 1.11. The fundamental structure and shape of the other nets are almost similar to the KITAHARA net.

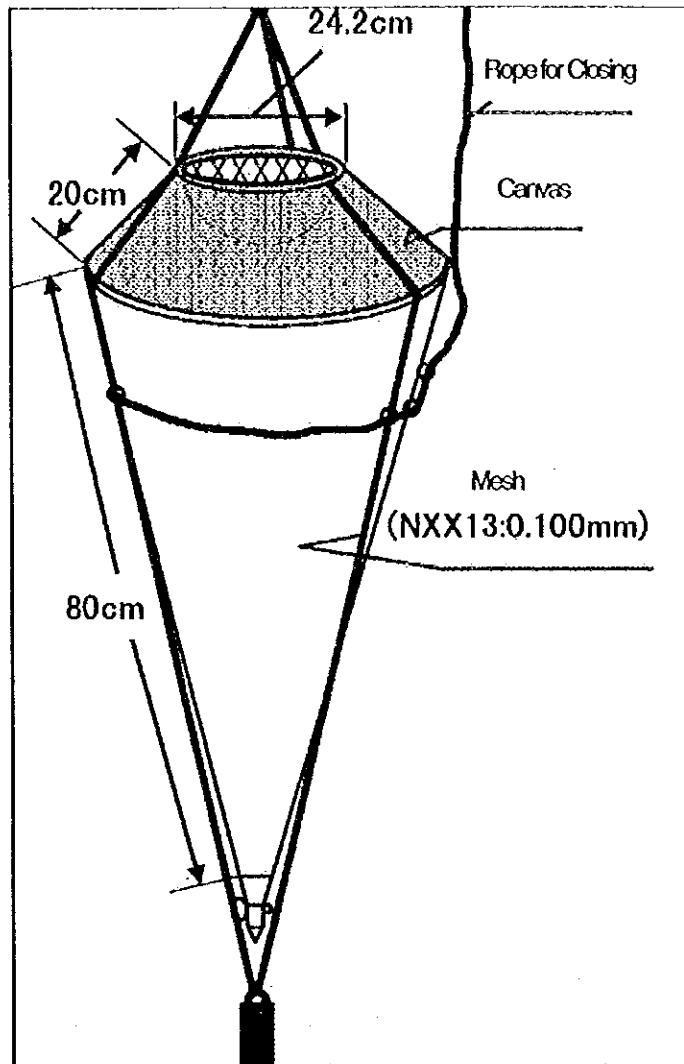


Figure 1.11 Drawing of a KITAHARA Plankton Net

Plankton sampling by net is carried out in three ways, as shown in Table 1.8.

Table 1.8 Method of Plankton Net Sampling

1	Vertical Haul
2	Horizontal Haul
3	Oblique Haul

## 1.7.2 Plankton Survey by Net Method

### (1) Vertical Hauling Method

Zooplankton is found at different layers at any given time because of vertical migration. When there is a need to compare the different layers, a closed type of plankton net should be used. In measuring water volume, use a flow meter, shown in Figure 1.11, to measure filtration volume.

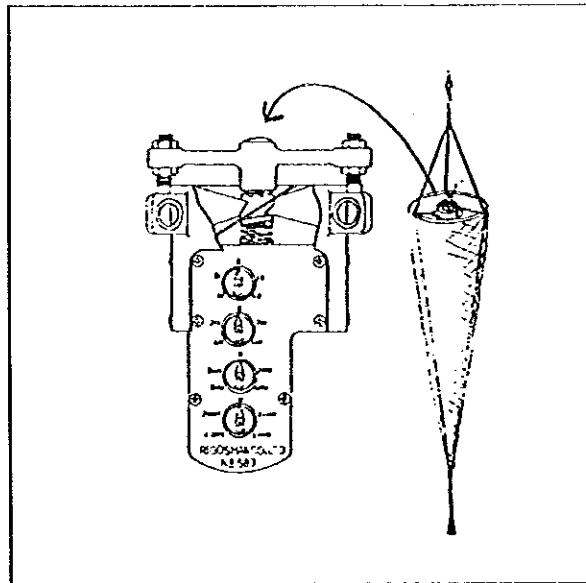


Figure 1.12 Picture of a Flow Meter

The plankton net is hauled vertically when the ship is at anchor. A one to two-kilogram weight is attached to the net.

Plankton survey by vertical hauling is accomplished in the following manner:

- 1 Calibrate and lock the flow meter before hauling
- 2 Unlock the flow meter
- 3 Slowly lower the net to the target depth, and then haul it in at a velocity of 0.5–1 m/sec
- 4 Drop a messenger to close the mouth
- 5 Drain the net after hauling, record the filtering coefficient on the flow meter, and then open the bucket cock to transfer the collected sample to a sample bottle
- 6 Close the bucket cock, wash the net with seawater from outside of the filter tube, and once again, transfer the samples from the bucket to the bottle
- 7 Repeat this at least two times
- 8 Immediately after transferring the plankton samples to the sample bottles, add formalin to preserve 5% to 10% of the total sample volume

## (2) Horizontal Hauling and Oblique Hauling

When no plankton exists in a water body, such as an open sea area, for biological analysis, sampling by horizontal hauling will be done. The sampling method is as follows:

- Drop the plankton net into the water; leave it over 10 m from a boat (direction depends on size of the boat)
- Haul the net at below 2 knots for 15 to 30 minutes

In case of plankton sampling in the middle layer, oblique hauling is used. The MTD net (Modern Top Design Net), shown in Figure 1.12, is widely used. It has a triangular frame at its top and its mouth closes underwater after hauling.

Multiple attachment of the aforementioned device on one line enables the simultaneous sampling at different layers.

- 1 Calibrate and lock the flow meter before hauling.
- 2 For the actual manipulation, the net is

hauled from the stern of a boat for at least 30 minutes. A disadvantage of this simple method is that a considerable amount of sample organisms might be destroyed by the time of observation.

### 1.7.3 Fixation

Like any other organic sampling, the fresher the plankton samples, the better. However, plankton samples need to be stored for a considerable length of time until they are actually inspected. For the fixation, neutral formalin delivers the best effect at a concentration of 3% to 10% of total volume of sample.

### 1.7.4 Pretreatment

Plankton samples should be concentrated so that they could easily be observed by microscope. The following two method are commonly used.

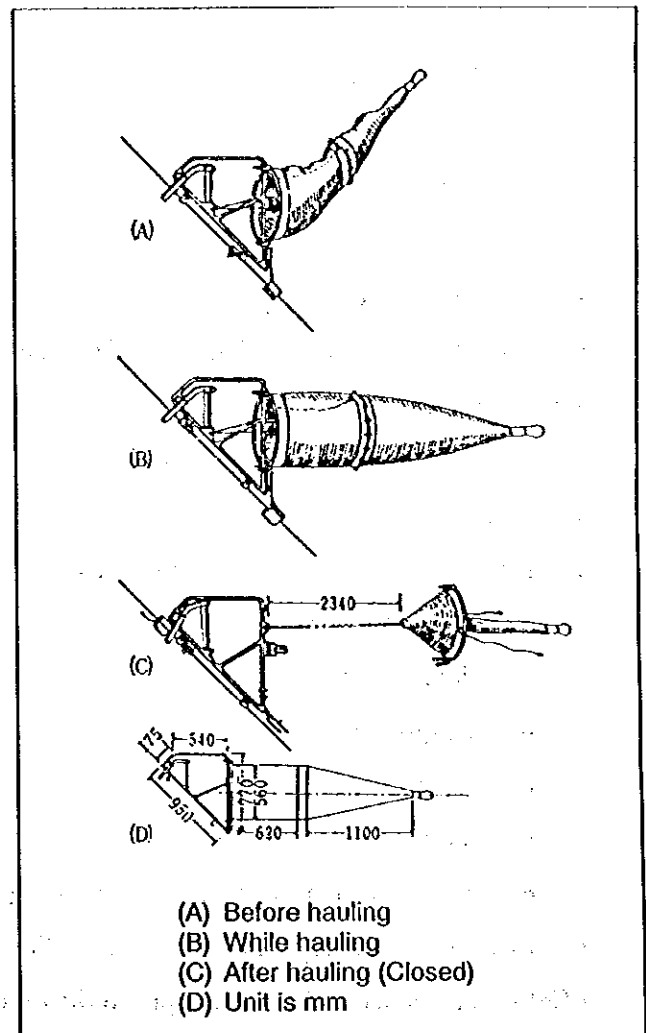


Figure 1.13 Picture of MTD Net

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- Centrifugation method: Samples are centrifuged for 15 minutes at 2500 rpm.
  - Sedimentation method: Samples are let to stand for 24 hours and concentrated by drawing out the supernatal.

### **1.8 Field Notes**

Field notes contain a checklist to confirm that all the necessary equipment for the survey are available and in good working condition, and observations during the actual field survey, which can provide invaluable information in analysis, preparation of report and future surveys.

The following information should be written down on field notes:

- sampling date;
- field name;
- sampling point;
- sampling layer;
- sample bottles; and
- other information such as surrounding environment.

The location, frequency and quantity of sediment sampling should always be written down in a field note. Since sediment samples oxidize, darken and deteriorate fast, this process should be duly noted in terms of time, color and odor. Appearance of sediment samples should be noted based on the following types: gravel, sand, silt and mud.

### **1.9 Maintenance of Equipment**

It is necessary to wash the equipment after sampling, because salt water causes rust and other operational problems. Washing should be done carefully because some parts may be inadvertently moved or switched on.

### **1.10 Safety Measures**

Conditions in coastal areas greatly differ from those in rivers, lakes and lagoons. There are wind waves and swelling to consider. Since sea conditions could easily change, careful attention should be paid when conducting field surveys in coastal waters. The following should be taken into account:

- Obtain forecast weather information;
- Prepare lifejackets;



- 
- Bring a radio communication equipment; and
  - Keep careful watch of other boats and submerged rocks to avoid collision.



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## Chapter 2 Method for Seawater Analysis

### 2.1 Introduction

The analysis of chemical parameters for water quality monitoring of seawater and river water is not much different from the analysis of lake water, underground water and industrial wastewater when it comes to matrix content. Chemical data, which measure concentrations of pollutants and other chemical conditions that influence aquatic life, i.e., acidity and dissolved oxygen concentrations, may be analyzed in water samples, sediment samples, and biological tissue samples.

Standard methods like those by the U.S. Environmental Protection Agency (EPA) and Japan Industrial Standard (JIS) are not specifically established for seawater analysis, although they may be used as references. There are, however, many handbooks written on seawater analysis like the one called "A Practical Handbook of Seawater Analysis" (J.D.H.Strickland and T.R.Parsons, 1972). The Environmental Agency of Japan has also published some handbooks on seawater and sediment analysis

What is important is to choose the most appropriate standard considering environmental conditions in the subject coastal area.

### 2.2 Characteristics of Seawater Analysis

The analysis method of seawater and fresh water is essentially the same. The method used in seawater analysis is examined according to the following three standards:

- U.S. Environmental Protection Agency (EPA);
- A Practical Handbook of Seawater Analysis (PHSA); and
- Japan Industrial Standard (JIS).

Seawater has two significant characteristics: (1) it contains a large amount of chloride ions, and (2) it has low parameter concentration, which poses difficulty in measurement. Prior to analysis, it is necessary to remove the salt content of seawater sample. If this is not possible, the analysis method employed must be one in which the result is unaffected by chloride ions. For instance, the acidity of potassium permanganate method of COD is changed by adding silver nitrate the amount of which corresponds to the amount of chloride ions present in the sample. This will trigger precipitation of silver chloride, thus eliminating the chloride ions. Also, the alkaline potassium permanganate method of COD is protected from interference of

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chloride ions because of oxidation under alkaline condition. This method is widely used for analysis of COD in Japan.

There are several methods to determine the composition of low parameter concentration. The most common method is by condensing, which changes the measuring component from saline water to solvent of a few volume. Atomic absorption meter and gas chromatography are largely used to analyze the objective component extracted from the solvent. Thus the extracting procedure removes chloride ions as well as condenses the objective component.

There are some methods that could condense water samples through a column with packing ion exchange resin. The objective components absorbed by the resin could be extracted by adding some acid. However, this procedure is time consuming and involves a series of operating processes, raising the possibility of contamination. Extreme care should be taken especially when washing the glass tools to be used; dust should be minimized during this activity.

It is desirable that routine work, like water quality monitoring, be kept simple but effective. One way to accomplish this is to heighten the sensibility of measuring apparatus. For instance, when using a spectrophotometer to measure the concentration of phosphate phosphorus, no less than a 50-mm cell of light path should be used. Superior sensibility is attained from fluorophotometer to spectrophotometer in the measurement of chlorophyll-a. The former can measure a sample of lesser concentrations and volume than the latter.

As a final word on chemical analysis, strive to obtain a low value result as much as possible when conducting a blank test.

Methods for seawater analysis are shown in Table 2.1

Table 2.1(1) List of Methods for Seawater Analysis

	Parameter	Method	Reference
Basic Parameters	Transparency	Secchi disc on boat	
	Water temperature	STD on boat	
	Salinity	STD on boat	
	pH	Glass electrode method	JIS K 0102 12, EPA 150.1
	DO	Winkler-sodium azide modification	PHSA I-3, JIS K 0102 32.1
	COD	Alkaline-iodine method	JIS K 0102 19
	TOC*	Non-purgeable organic carbon method	JIS K 0102 22, EPA 415.1 By TOC Analyzer
	SS	Gravimetric method	JIS K 0102 14.1
	NH <sub>4</sub> -N	Indophenol blue absorptiometry	PHSA II-9
	NO <sub>2</sub> -N	Naphthylethlen diamine absorptiometry	PHSA II-7, JIS K 0102 43.1, EPA 354.1
	NO <sub>3</sub> -N	Cd-Cu column reduction method	PHSA II-6, JIS K 0102 43.2, EPA 353.3
	T-N	Cd-Cu column reduction method	JIS K 0102 45.4
	PO <sub>4</sub> -P	Molybdenum blue absorptiometry	JIS K 0102 46.1, PHSA II-2
	T-P	Molybdenum blue absorptiometry	JIS K 0102 46.3
	Chlorophyll-a	Spectrophotometric determination	PHSA IV-3-1
Total coliform, Fecal coliform	Membrane filter method	SMEWW922A, 922D	
Toxic Parameters	Hexane extracts	Liquid-liquid extraction, Gravimetric Method	JIS K 0102 24
	Phenols	4-aminoantipyrine absorptiometry	JIS K 0102 28.1.2
	Cyanide	4-pyridine carboxylic acid-pyrazolone absorptiometry	JIS K 0102 38
	Cr	Diphenylcarbazide absorptiometry	JIS K 0102 65.1.1
	Cr <sup>6+</sup>	Diphenylcarbazide absorptiometry	JIS K 0102 65.2.1, EPA 7196A
	Cd	Atomic absorption spectrometry	JIS K 0102 55, EPA 7131A
	Pb	Atomic absorption spectrometry	JIS K 0102 54, EPA 7421
	Cu	Atomic absorption spectrometry	JIS K 0102 52, EPA 7211
	Zn	Atomic absorption spectrometry	JIS K 0102 53, EPA 7521
	Ni	Atomic absorption spectrometry	JIS K 0102 59, EPA 7951
As	Atomic absorption spectrometry using hydride system	JIS K 0102 61.2, EPA 7062	

Table 2.1(2) List of Methods for Seawater Analysis

Parameter	Method	Reference
T-Hg	Atomic absorption spectrometry using vapor reduction system	JIS K 0102 66.1, EPA 7470A
Alkyl-mercury	Gas chromatography with ECD	JIS K 0102 66.2
Organo phosphorus	Gas chromatography with FID	Notification No. 46 <sup>(1)</sup>
Trichloroethylene	Gas chromatography with ECD	JIS K 01025 5.5, EPA 8021B
Tetrachloroethylene	Gas chromatography with ECD	JIS K 01025 5.5, EPA 8021B
Carbon tetrachloride	Gas chromatography with ECD	JIS K 01025 5.5, EPA 8021B
PCB	Gas chromatography with ECD	EPA 8082, JIS K 0093 (Pretreatment)
HCB	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>
Aldrin	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>
Endrin	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>
Dieldrin	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>
DDT	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>
Chlordane	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>

Notes:

- STD : Salinity, Temperature, Depth Measuring System
- PHSA : A Practical Handbook on Seawater Analysis
- JIS : Japan Industrial Standard
- SMEWW : Standard Method for Examination of Water and Wastewater
- EPA : Environmental Protection Agency

(1) Notification No. 46, 1971 of Japan Environmental Agency

(2) Tentative Survey Manual of External Factor Endocrine Disturbance Chemical Substance

\*TOC was analyzed in dry season.

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### 2.3 Characteristics of Sediment Analysis

The method of analysis for sediment samples is similar to other soil types, except for samples taken from hydrosphere. The method used in sediment analysis is examined according to the following three standards:

- U.S. Environmental Protection Agency (EPA);
- The Handbook of Bottom Sediment Survey (HBSS); and
- The Method of Analysis Guideline of Water Pollution (MAGWP).

The Japanese standards (HBSS and MAGWP) are good for analysis of soil, especially bottom sediment in hydrosphere.

Sediment samples are characterized by the following:

- Bottom sediment contains much water; and
- Bottom conditions are of various types.

Generally, the unit of sediment analysis is indicated by the amount per dried weight. Therefore, water content is first calculated using the following formula:

$$\text{Water Content (\%)} = \frac{W_0 - W_1}{W_0} \times 100$$

where:

W<sub>0</sub> : Weight of wet sediment

W<sub>1</sub> : Weight of dried sediment

For example, if water content is 50%, 100 g of wet sample is only 50 g of dried sample.

Water content is dependent on bottom conditions. Silt contains much water; occasionally, water content reaches over 90%. In the case of coastal areas, its salty water, called pore water, sometimes influence the analysis of sediment samples taken thereat. Pore water should be eliminated as much as possible. The general method for elimination of pore water is by centrifugation. This process separates pore water from sediment samples by centrifuging at 3,000 rpm for 20 minutes.

It is difficult to homogenize wet sediment sample because they contain various particle sizes. In case a method is used that requires just a small amount of sediment sample, e.g. TOC or heavy metal analysis, the results may be uneven.

To homogenize the sample, the following procedure is followed:

- Dry the sample in a oven at 100 to 110 °C (or air dry) temperature
- Grind down the dried sample
- (Sieve) and mix it to homogenize

The condition of sediment depends on the condition of its location. Sediment in a stagnated area, contains much silt and organic matters, and become like sludge. That found near the shore, where water movement is comparatively large, is sandy. In general, smaller sediment sample is better as it tends to contain organic matters, heavy metals and so on.

An elution test aims to measure the amount of eluted toxic substances from sediment samples.

Liquid sample for elution test is made by the following procedure.

1. 500 ml of water and 3 % of sediment sample are mixed and shaken for six hours
2. Separate water by decantation or filtration

Liquid sample can be analyzed by the same method of analysis for water quality.

Methods for sediment analysis are shown in Table 2.2

Table 2.2 (1) List of Methods for Sediment Analysis

	Parameter	Method	Reference
Content Test Basic Parameter	Particle Size	Separation method with sieve	
	ORP	Glass-electrode method on boat	
	Ignition Loss	Gravimetric Method at 600 °C	HBSS II.4
	COD	Alkaline-iodine method	MAGWP 5.11
	TOC	Dry-decomposition method – non-purgeable organic carbon	By TOC Analyzer
	Sulfide	Heating Distillation Method	MAGWP 5.11
Toxic Parameter	Hexane extracts	Liquid-liquid extraction, Gravimetric method	EPA 9071A (Use hexane), MAGWP 5.11
	Cyanide	4-Pyridine carboxylic acid - pyrazolone absorptiometry	HBSS II.14
	Cr	Acid digestion, Diphenylcarbazide absorptiometry	HBSS II.12.1, EPA 3050B, 3052 (Pretreatment)
	Cd	Acid digestion, Atomic absorption spectrometry	EPA 3050B (Digestion), HBSS II.6, EPA 7131A
	Pb	Acid digestion, Atomic absorption spectrometry	EPA 3050B (Digestion), HBSS II.7, EPA 7421
	Cu	Acid digestion, Atomic absorption spectrometry	EPA 3050B (Digestion), HBSS II.8, EPA 7211
	Zn	Acid digestion, Atomic absorption spectrometry	EPA 3050B (Digestion), HBSS II.9, EPA 7951
	As	Acid digestion, Atomic absorption spectrometry using hydride system	EPA 3050B (Digestion), HBSS II.13



Table 2.2(2) List of Method for Sediment Analysis

	Parameter	Method	Reference
Toxic Parameters	Alkyl-mercury	Gas chromatography with ECD	JIS K 0102 66.2, Notification No. 127 <sup>(3)</sup>
	Organophosphorus	Gas chromatography with FID	Notification No. 46 <sup>(1)</sup>
	Trichloroethylene	Gas chromatography with ECD	JJIS K 0125 5.5, EPA 8021B, Notification No. 46 <sup>(1)</sup>
	Tetrachloroethylene	Gas chromatography with ECD	JJIS K 0125 5.5, EPA 8021B, Notification No. 46 <sup>(1)</sup>
	Carbon tetrachloride	Gas chromatography with ECD	JJIS K 0125 5.5, EPA 8021B, Notification No. 46 <sup>(1)</sup>
	PCB	Gas chromatography with ECD	JJIS K 0093, EPA 8082, Notification No. 127 <sup>(3)</sup>
	HCB	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>
	Aldrin	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>
	Endrin	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>
	Dieldrin	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>
	DDT	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>
	Chlordane	Gas chromatography with ECD	EPA 8081A, Tentative Survey Manual <sup>(2)</sup>
Elution Test	Hexane extracts	Liquid-liquid extraction, Gravimetric method	JIS K 0102 24
	Cyanide	Pyridine-pyrazolone absorptiometry	JIS K 0102 38
	Cr <sup>6+</sup>	Diphenylcarbazide absorptiometry	JIS K 0102 65.2.1, EPA
	Cd	Atomic absorption spectrometry	JIS K 0102 55, EPA 7131A
	Pb	Atomic absorption spectrometry	JIS K 0102 54, EPA 7421
	Cu	Atomic absorption spectrometry	JIS K 0102 52, EPA 7211
	Zn	Atomic absorption spectrometry	JIS K 0102 53, EPA 7521
	As	Atomic absorption spectrometry using hydride system	JIS K 0102 61.2, EPA 7062
	T-Hg	Atomic absorption spectrometry using vapor reduction system	JIS K 0102 66.1, EPA 7470A
	Alkyl-mercury	Gas chromatography with ECD	JIS K 0102 66.2
	Organophosphorus	Gas chromatography with FID	Notification No. 46 <sup>(1)</sup>
	PCB	Gas chromatography with ECD	EPA 8082, JIS K 0093 (Pretreatment)

Notes:

HBSS : The Handbook of Bottom Sediment Survey; Japanese Standard

JIS : Japan Industrial Standard

EPA : Environmental Protection Agency

MGAWP: The Method of Analysis Guidelines of Water Pollution

(1) Notification No. 46, 1971 of the Japanese Environmental Agency

(2) Tentative Survey Manual of External Factor Endocrine Disturbance Chemical Substance

(3) Notification No. 127 issued by Water Quality Control Section, Water Protection Department, EPA

TOC was analyzed in dry season.

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## 2.4 Characteristics of Biological Accumulation Test

In the assessment of environmental quality, it is important to measure the health of aquatic communities, as they may affect the health of the people. Thus, a biological accumulation test is to be conducted after drawing up an appropriate plan and method to be applied on representative species in the water bodies. A rough procedure of biological accumulation test includes: (1) sampling; (2) pretreatment; and (3) analysis.

### 2.4.1 Sampling

Biological data to be recorded should include sampling date, area, and species. If the sample was a fish, its length, weight, sex and, if possible, age, should be recorded. The species to be sampled should take into account the trophic level and food chain existing within its ecosystem. Furthermore, it should be representative of the monitoring area.

The prescribed number of samples is over 5 for the same area and species; it may be necessary to conduct regression analysis in some cases.

### 2.4.2 Pretreatment

The separation of sample body will depend on the analysis objective. A biological sample is considered to have the following three parts;

1. Whole body,
2. Muscle and meat, and
3. Internal organs.

The whole body of small-bodied samples, like the plankton, is usually analyzed. On the other hand, fish and shell samples are separated into parts. In this study, as their influence on human food is to be studied, the muscle of fish sample and the whole body of oyster sample were used for the test.

The next step is to further cut the separated parts of the samples into small pieces and homogenize them using a mixer or homogenizer.

Dry sample is used for analysis of heavy metals. In this regard, it would be better to use a 'freeze and vacuum drying method,' because using an oven would produce a foul-smelling sample.

### 2.4.3 Analysis

The analysis method of biological accumulation test and that of sediment samples are fundamentally the same, as discussed in Chapter 2.3. In the case of biological accumulation

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test, it is the rich organic matter, e.g. fat, which can disturb some analysis, like those for heavy metals and analysis by gas chromatographic method.

A method of digestion for heavy metal analysis is usually by acid digestion, the same as that for sediment analysis. Ashing process, however, is required before acid dissolution in order to decompose organic matters. The most common way to do this is to ignite the sample in an oven at a temperature of 600 °C.

The usual method of extracting organic compounds, e.g. pesticides and PCB, is by liquid-liquid extraction; an emulsion results from samples containing numerous organic matters. In this case, it would be better to use a Soxhlet extractor for extraction.

Acid digestion or alkaline saponification is an effective method to remove interfering matters from extracted sample before proceeding with cleaning procedure by means of column chromatography.



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## Chapter 3    Laboratory and Data Management for Water Quality Monitoring

### 3.1    Laboratory Management

Laboratory Management is made up of six components, as follows:

- Organizational structure,
- Building and facilities,
- Reagent management,
- Wastewater management and solid waste management,
- Safety and sanitation, and
- Equipment management.

#### 3.1.1    Organizational Structure

Three sections shall be established in a Regional Laboratory; namely, Administration Section, Planning Section and Sampling/Analysis Section, as shown in Figure 3.1 and Table 3.1. A Head shall be appointed to supervise a Regional Laboratory. The Administration Section shall be responsible for administrative matters pertaining to the management of the laboratory, including the Monitoring Site Office. The Planning Section, which shall handle monitoring plans and data management for coastal areas, shall prepare and submit monitoring reports, among other documents, to Tampico Core Center. The Sampling/Analysis Section shall implement water quality monitoring, including preparatory activities. This section shall also be responsible for the maintenance of monitoring equipment for sampling and analysis.

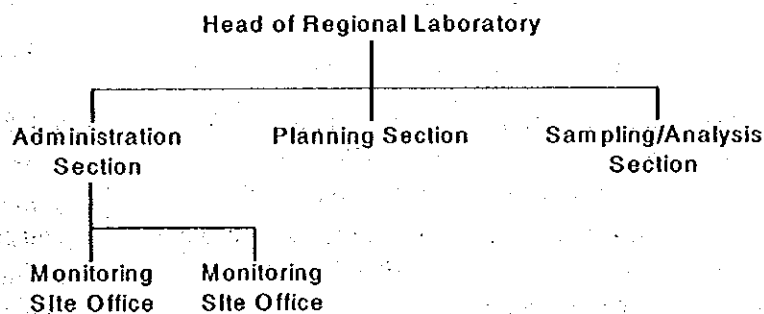


Figure 3.1    Proposed Organizational Chart of a Regional Laboratory

In order to carry out a continuous water quality monitoring, with accurate data output, the Regional Laboratory Head should take note of the following points:

- (1) Set up a simple organizational structure consisting of the fewest number of management personnel as possible.
- (2) Although the Laboratory Head would be in charge of overall management, it is desirable to delegate work and responsibility to section heads. It is therefore important that the section heads be responsible and competent people.
- (3) There should be flexibility in organizational structure such that important tasks are not concentrated in only one person. For example, the responsible person for appraisal of analytical results, for equipment management, and for health and security should be able to share their tasks to another staff outside of line administrative position.
- (4) It is advisable to appoint a person in charge and an assistant/s for each analytical parameter. In this way, several people would be knowledgeable in the analysis of the particular parameter and ensure uniformity of analytical technique.
- (5) It is important to provide further training to analytical specialists in order to enhance their water quality monitoring skills; other personnel who have the potential for such work should be given equal opportunity to attend training programs on water quality monitoring. This would serve as motivation to perform their jobs well, with the thought of career advancement in the future.

Table 3.1 Functions of the Different Sections in a Regional Laboratory

Sections	Administration Section	Planning Section	Sampling/Analysis Section
Functions	<ul style="list-style-type: none"> <li>• to manage building and facilities</li> <li>• to manage personnel</li> <li>• to manage budget and accounting</li> <li>• to manage monitoring equipment</li> <li>• to manage laboratory property</li> <li>• to control Monitoring Site Offices</li> </ul>	<ul style="list-style-type: none"> <li>• to prepare plan for monitoring</li> <li>• to compile data</li> <li>• to prepare monitoring reports</li> </ul>	<ul style="list-style-type: none"> <li>• to take samples</li> <li>• to analyze sample</li> <li>• to maintain monitoring equipment</li> <li>• to manage quality control</li> </ul>

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- (6) In order to avoid a one-sided performance appraisal of staff, it is advisable to introduce a self-appraisal system. In this way, the supervisors get to meet with their staff and discuss their individual assignments. Each staff member sets a performance target for the year, and then assesses his/her performance at the end of the year.
  - (7) Periodic exchange of laboratory and administrative personnel between central and regional laboratories is recommended to strengthen their link and to create a “fresh” environment in laboratory work.

### 3.1.2 Building and Basic Facilities

#### (1) Building

The proposed design concept of the Regional Laboratory is shown in Table 3.2. The required area for a Regional Laboratory building is 1,000 m<sup>2</sup> with 5 to 6 laboratory rooms of 50 to 60 m<sup>2</sup> each.

The air conditioning in the building should be controlled in order to maintain the appropriate temperature and measurement of dust in the laboratory rooms. Since sunlight affects analysis activities and laboratory equipment, the windows of laboratory rooms should have shades. Inside laboratory rooms, side tables are to be placed at corners with provision of gas tube, electricity, and water supply and drainage. A main analytical table should be placed at the center of the room with the same provision. The distance between the main table and corner tables should allow room for two persons to work comfortably.

#### (2) Basic Facilities

Installation of the following basic facilities to carry out routine work is required:

- Electricity,
- Gas,
- Water supply,
- Wastewater and solid waste treatment facilities,
- Research vessels,
- Automobile,
- Air conditioner,
- Telephone and Fax, and
- Copy machine.

### (3) Management of Building and Basic Facilities

The responsibilities of the person in charge of maintenance and management of laboratory building and facilities include the following:

- a) To ensure that the building and facilities are kept in good condition. This includes carrying out periodic safety inspections, inventory of supplies and repair/replacement of broken down or obsolescent parts;
- b) To secure the building and facilities against burglary and other crimes; and
- c) To keep a ledger of the management activities and building repairs for future reference.

Table 3.2 Design Concept of Laboratory Building

Items	Requirement
Size of area	1,000 m <sup>2</sup> and parking area
Room Arrangement	<ol style="list-style-type: none"> <li>(1) Room(s) for analyses of basic parameters (filtration of samples, analyses of COD and DO etc.)</li> <li>(2) Room(s) for decomposition of organic substances as a pretreatment of analyses</li> <li>(3) Room(s) for extraction processes with solvents</li> <li>(4) Room(s) for instrumental analyses (Spectrophotometer, TOC analyzer, auto-analyzer, Atomic absorption spectrometer, Gas chromatograph)</li> <li>(5) Room(s) for analyses of basic parameters for sediments (particle size, ignition loss, specific gravity etc.)</li> <li>(6) Room(s) for bacteria, biochemical and bacteriological analyses</li> <li>(7) Room(s) for microbalances, which are placed on the anti-shock table, under controlled temperature</li> <li>(8) Room(s) for storage of samples</li> <li>(9) Room(s) for management and staff</li> <li>(10) Meeting room</li> <li>(11) Library</li> </ol>
Laboratory Infrastructure	<ol style="list-style-type: none"> <li>(1) suitable electricity</li> <li>(2) water supply with appropriate water pressure</li> <li>(3) air conditioner</li> <li>(4) appropriate light (avoid direct sunlight from outside)</li> </ol>
Laboratory Facilities	<ol style="list-style-type: none"> <li>(1) laboratory waste bins (for separation of laboratory equipment)</li> <li>(2) laboratory wastewater treatment facilities</li> </ol>



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### 3.1.3 Reagent Management

Analysis work should be carefully done in order to avoid contamination of samples or deterioration of reagents, which could lead to incorrect data. Reagents should be strictly managed and carefully handled because some of them are combustible.

#### (1) Responsible Person

The person in charge of Sampling/Analysis is responsible for the proper storage and use of reagents in order to prevent accidents.

#### (2) Storage of Reagents

Reagents should be stored in a cool dark place. Preferably, the reagents should be kept in earthquake-proof shelves or cabinets in a storage room, where there are fire extinguishers. The storage room should be locked, and the key kept by the responsible person who shall control the reagents in stock.

#### (3) Procedure for Receiving Analytical Reagents from Storage

The person in-charge of Sampling/Analysis should approve all requests for reagents from analysts. Any withdrawal of reagents from stock should be properly recorded in a Reagent Management Recording Book, as shown in Figure 3.2.

#### (4) Standard Solution

A standard solution to be used, like for pH calibration, must be certified as a component. A label is to be pasted on the bottle of a standard solution prepared from reagent, with the necessary information written on it like the preparation date, the factor and expiration date, etc.

#### (5) Water

The appropriate water (pure water, distilled water, ion exchange water) to be used for a particular analysis work should be referred to a water standard (in Japan, JIS K 0557). Avoid using water that has been stored for a long period of time.

#### (6) Purchase and Disposal

The laboratory should be well stocked with supplies considering the rate of consumption. An inventory should also be made so that expired reagents are disposed of as soon as possible. The method of disposal should conform with existing ordinance of the area.

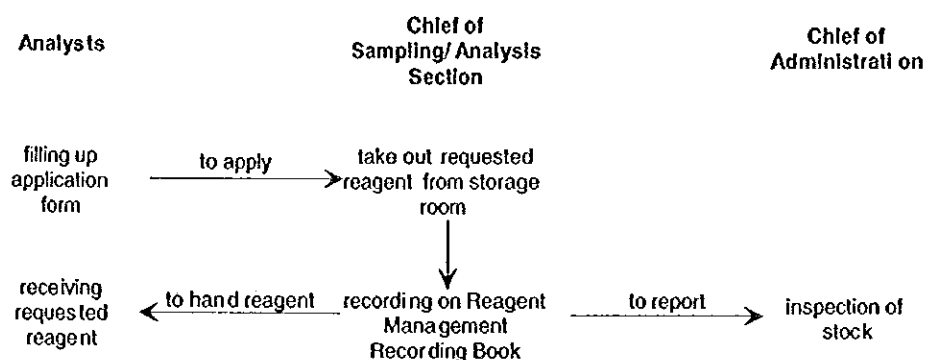


Figure 3.2 Procedure of Request for Analytical Reagent

### 3.1.4 Wastewater Management and Solid Waste Management

#### (1) Policy of Wastewater Management

It is ironic that water pollutants, which are analyzed in the laboratory as part of environmental monitoring, are subsequently discharged. In the conduct of analysis, therefore, the following two points are considered:

- The use of toxic substances is to be limited to the extent possible.
- The discharge of waste is to be kept at a minimum.

With the above in mind, the following describes the management of pollutants from a chemical laboratory.

#### a) Reduction of pollutants

In the analysis of pollutants, various reagents are used, including toxic matter. It is important to reduce the quantity of reagents by considering the following two points:

- To reduce toxic reagents

A most effective way to reduce the use of reagents is to reduce the amount of sample for analysis. Therefore, it is better to use a highly sensitive method and equipment for analysis.

- Not to use toxic reagents

It is advisable to choose a method which would not require the use of toxic reagents. In the Study, ascorbic acid was used instead of tin chloride in the analysis of phosphate phosphorous and total phosphorous. Also, for analysis of COD, alkaline potassium permanganate was used instead of mercury chloride.

b) Non-discharge of pollutants

Waste substances taken out from the laboratory come in three forms:

- Gas,
- Solution, and
- Solid.

Processing corresponding to each form is required.

(2) Gaseous Waste

Gaseous waste mainly consists of acid steam and offensive odor. From the laboratory, passing through a vacuum system or the like, this gaseous waste is exhausted outside. An example of a generous exhaust system is shown in Figure 3.3.

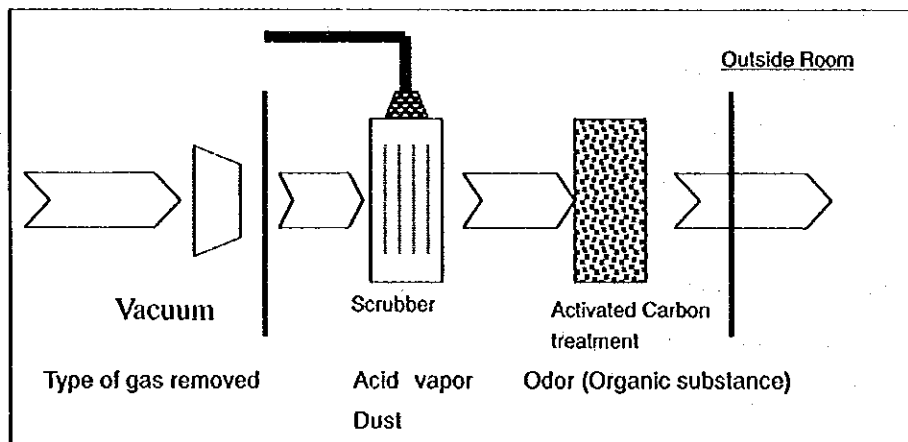


Figure 3.3 Example of Exhaust Ventilation System

Water washes out the acid steam, removing dust at the same time. Activated carbon treatments are necessary to completely remove dust, although organic substances that cause offensive odor are also partly removed.

It is most suitable to separate gas proportionately in a vacuum system according to type. However, it would be difficult to do this considering the cost involved as well as the size of the laboratory. As simple equipment, an activated carbon treatment system by which acid removal is possible is also to be developed and marketed.

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### (3) Wastewater

Waste discharge from a laboratory consists of organic solvent and aqueous solution. The treatment for organic solvent is comparatively simple since its toxicity is not so high, especially for a simple chemical compound of carbon, hydrogen and oxygen. Although the simplest method is incineration, this poses a threat to human health.

In recent years, studies have indicated that incineration of organochlorine compounds gives rise to the emission of dioxin, a deadly poison. The treatment of these waste materials in a laboratory is quite difficult; appropriate facilities would be required. It is necessary to store the chemicals until they are taken back to the facilities for processing. At the time of storage, it is extremely important to do the following:

- Separate waste solvent by kind.
- Use an appropriate vessel, preferably glass or metal, which a solvent cannot corrode/damage.
- Stock the chemicals safely in the storage house.
- Identify the chemicals as to used volume or stocked volume, because they differ in emission level to the environment.

Processing of aqueous solution should be carried out in proportion to each material contained therein. The solution is normally divided into the following:

- Acid and alkaline water,
- Wastewater including heavy metals,
- Wastewater including other inorganic matter, and
- Wastewater including organic matter.

A general procedure of wastewater treatment is shown in Figure 3.4. It involves the following three steps:

1<sup>st</sup> Step : Removal of heavy metals, etc.

2<sup>nd</sup> Step : Neutralization

3<sup>rd</sup> Step : Treatment with activated sludge (removal of organic substance)

Steps 1 and 2 are important, and these steps must be done in the laboratory. Regarding the 3<sup>rd</sup> step, as the volume of water and concentration of COD are not so high in comparison with general domestic wastewater, it would be possible to entrust a sewage treatment facility with wastewater treatment. But if the wastewater has high concentration of COD, and there is no

sewage treatment system, it would be necessary to use an activated sludge treatment system. It is desirable to connect the installation of wastewater treatment systems in order to closely watch and observe the treatment process; however, this is costly. Though it is desirable that a fractionation equipment be installed in the laboratory, manual processing could be done in the meantime. In this report, the activated sludge treatment system is too complicated to be examined in detail and would require further examination.

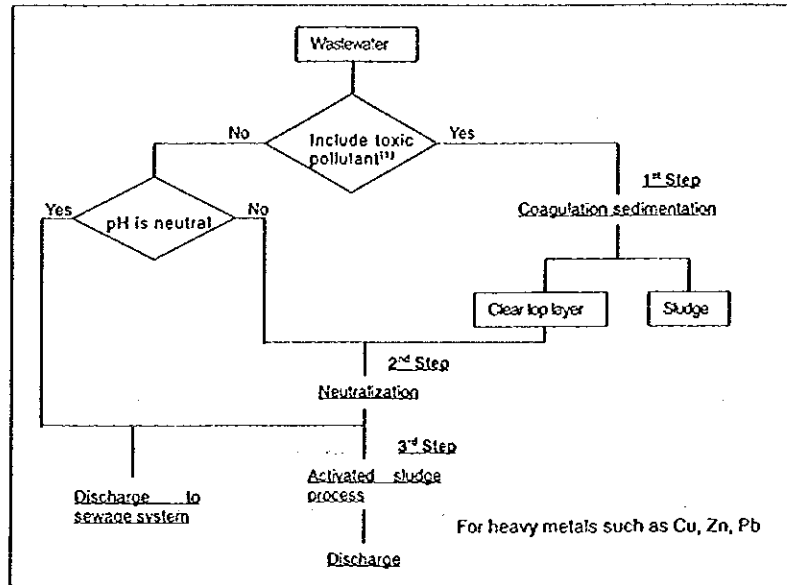


Figure 3.4 Example of Wastewater Treatment Procedure

Management of wastewater by type is discussed here independent of any other considerations. A concrete example of wastewater processing is shown in Table 3.3.

On wastewater management, attention should be given to the following:

- Recording of all processes, and
- Self-check of wastewater quality.

In the record of wastewater management, the following should be included:

- Date
- Type of wastewater (analytical parameter)
- Volume
- Method of treatment
- Name of person handling treatment and others

Samples of wastewater should be taken regularly in order to assess its condition and measure its toxicity. It is also desirable to measure some parameters, such as pH, which is easy to monitor.

Table 3.3 Example of Wastewater Processing

Type of wastewater	Procedure
Acid solution	Neutralize with alkaline water such as sodium hydroxide.
Alkaline solution	Neutralize with acid water such as hydrochloric acid
Heavy metal solution*	Chemical coprecipitation with another metal compound such as iron chloride.

\* Mercury is not included.

#### (4) Solid Waste

Solid waste is generally classified into two kinds:

- Remains of solid sample, and
- Sludge from removal process of heavy metals.

Most of the solid samples obtained in the environmental survey could be dumped because they contain low concentrations of toxic matter, such as heavy metals.

Solid samples, which are pretreated with organic solvent, acid or alkaline solution, could be dumped after washing with water.

It is possible to recycle sludge, minus any harmful heavy metal, as metal resource.

#### 3.1.5 Safety and Sanitation

The following points are to be carefully considered with regards to the safety and sanitation management of the laboratory:

- The Laboratory Head should appoint a person in charge of laboratory safety and sanitation, since laboratory personnel often handle dangerous and harmful substances in the performance of their duties.
- The person in charge of safety and sanitation should give proper notice on safety and sanitation procedures to the laboratory analysts. Also, the latter should report to the former any health concerns about the use of reagents and solvents.
- There might be a need to have a special room like a draft chamber where some harmful substances could be handled, and to install an exhaust system so that harmful gases generated during the operation could be fanned to the outside.

- 
- There should be countermeasures drawn up to address any worse eventualities that could occur when handling dangerous substances. Also, ordinary safety measures like the wearing of safety masks, safety glasses and use of safety pipette in common analysis should be put into practice.
  - The laboratory analysts should be given a medical checkup at least twice a year. Especially those who concentrate in the analysis of organic solvents like hexane should be periodically examined to determine the level of concentration of such substance in their blood.
  - Safety drills in case of emergency, such as earthquake, accident or fire should be examined beforehand, and all of the staff should participate in practice drills, which should be carried out once or twice a year. It is desirable that a Safety Manual be prepared to address this matter.
  - The results of health examinations of the laboratory analysts, as well as countermeasures and events concerning sanitation and safety should be stored for a limited time.

### 3.1.6 Equipment Management

#### (1) Management System

The Laboratory Head should appoint a person who will manage the facilities and equipment used for analysis and to keep them in good working condition.

The person in charge of facilities and equipment should make a list (including number, article name, purchase date, type, location, responsible person) of equipment in the laboratory (Table 3.5). Thereafter, the person in charge shall determine the facilities and equipment that will require daily inspection and prepare the necessary ledger (Table 3.6). These facilities and equipment shall be checked and inspected based on the items shown in Table 3.7, and a record of inspection shall be entered in a ledger. The checking of each facility and equipment is carried out based on the standard previously prepared (Table 3.8).

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(2) Daily Examination and Record of Use

The facility and equipment are to be examined and adjusted at the beginning of work. The facility and equipment are then certified accurate to measure, and the result is documented in the Record of Use of Facility and Equipment (Table 3.9). In case an abnormality is observed in the facility and equipment during the examination at the beginning of work, the use of the facility and equipment is given up and the repair of the facility and equipment are sought for. At the same time, the results are recorded in the Record of Facility and Equipment Maintenance, and are reported to the person in charge of facility and equipment maintenance. At the beginning of work, the facility and equipment are to be cleaned and examined in order to prevent deterioration and to find any abnormality.

(3) Periodical Examination

At regular intervals or as the person in charge of facility and equipment maintenance sees fit, the following work is to be carried out:

- Overhaul, replenishment and replacement of expendables in addition to daily examination at the beginning of work;
- Confirmation of performance (variance) of a facility (or meter); and
- Recording of results of periodical examination in the Table of Results for Periodical Examination and in the Record of Facility and Equipment Examination.

(4) Repair

In case that the facility or equipment was found to be defective during an examination or actual use, the manufacturer or its selling agent should be asked to have them repaired, and at the same time, the results written in a Facility and Equipment Maintenance Record and reported to the person in charge of facility and equipment maintenance.

(5) Performance Examination

On items which cannot be covered in the periodical examination of a facility and equipment, their performance examination is asked to its producer or examination services in order to grasp the condition of the facility and equipment. A facility and equipment should be overhauled as needed in order to keep its condition good and its precision high.



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**(6) Official Examination**

Official Examinations prescribed by law and regulations should be carried out without exception, and results of official examinations are to be written in the Record of Facility and Equipment Maintenance.

**(7) Storage of Record**

The Record of Facility and Equipment Maintenance is to be stored for the period when it is held, while the other records are to be stored for two years.

**(8) Storage or Setting of Equipment**

Facility and equipment should always be stored or set in an appropriate place for use in order to prevent their contamination from indoor environment. A label, on which a record number is written, should be pasted on each item as an indication of a "maintained facility or equipment."

**(9) Maintenance of Instruments**

The precision of instruments that are commonly used is to be certified at need. Especially, volumetric instruments (measuring cylinder, pipettes and others) which are of JIS standard should be used. It is necessary that accurate measuring be tried. Washing, drying, and storing of instruments should be done with the appropriate method for each analysis, and it is necessary to keep the instruments clean in order to prevent contamination of samples.

**3.2 Data Management**

**3.2.1 Set up a Standard Operation Process (SOP)**

It is necessary to set up a simple but concrete processing of the following items, and, more importantly, to orient the persons concerned:

- Sampling, preparation and custody of reagent for pretreatment;
- Preparation of analytical reagent and standard solution, and custody and treatment of standard solution;
- Setting and adjustment of measuring conditions for analytical instrument; and
- Recording of whole measuring process.

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### 3.2.2 Preparation of Analysis and Evaluation of Efficiency of Apparatus

- Standard solution

It is necessary to use guaranteed material to ensure traceability.

- Pretreatment/Condensation

It is necessary to take suitable pretreatment operations since this affects the results of analysis. Collection test is also necessary after addition to confirm efficiency of previous collection.

- Adjustment of analytical equipment

Measuring conditions should correspond to samples, and instruments are to be adjusted accordingly. In those cases, it is necessary to confirm linearity of sensibility, stability, interference and faculty of adjustment.

### 3.2.3 Evaluation of Credibility of Measuring Results

#### (1) Detection Limit

There is a need to confirm whether the method used is able to clear minimum detection limit before beginning the chemical analysis by the following process. If it were unable to do so, it would be necessary to increase sample volume or to condense the sample some more.

- a) In the case where the object substance was detected

Measure seven operation blanks and calculate the amount in blank samples.

$$\text{Minimum detection limit (DL)} = x + 1.94 S$$

x: mean of blanks, S: standard deviation

- b) In the case where the object substance was not detected

Carry out the collection test seven times after adding the object substance into the distilled water at 2-5 times the lowest concentration for calibration. Calculate the minimum detection limit from standard deviation(s)

$$\text{DL} = 1.94 S$$

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(2) Operation Blank

It is necessary to measure the operation blank in order to confirm the contamination amount due to sampling, preparation of reagent and other handling activities. The measuring environment should be set in such a way that nothing interferes with the analysis. In case a high blank value is obtained, it would lead not only to the downslide of measuring sensibility but also to the decline of credibility of measuring result. Consequently, there is a need to bring down the value of operation blank to the extent possible and to measure the operation blank once every ten samples.

(3) Repeat Measurement

It is necessary to repeat the measurement once for each of the ten samples to confirm that the difference between the two measuring results is below 30% the average for substances over detection limit. When the difference is larger than 30%, there is a need to check the cause and measure again.

$$(C1-C2) \div (C1+C2) / 2 \times 100 \leq 30$$

(4) Daily Check on Sensitivity of Measuring Apparatus

The sensitivity of measuring equipment should be checked by means of measuring test sample of standard solution once every 10 samples, and confirm that the reduction of sensitivity is within 20% of previous standard solution. When the change is over 20%, there is a need to determine the cause, eliminate the cause and retest the equipment before measuring actual samples.

(5) Addition and Collection Test

It is necessary to take a collection test 3-5 times with the same samples after adding a suitable amount of known standard solution. It is desirable to have about 10 times concentration for detection limit.

(6) Confirmation of Accuracy by Cross-checking

There is a need to confirm analytical accuracy by cross-checking with other laboratories, and discussing with them the results and cause of any errors.

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### 3.2.4 Data Control and Evaluation

#### (1) Attention on Sampling

There is a need to confirm whether the water samples are suitable for the purpose of the survey and are representative of the sampling place.

#### (2) Treatment of Abnormal Data

If a drastic reduction in the sensitivity of measuring instruments occurs or the result of the second measurement varies widely with the first measurement, it means that the credibility of analysis has become questionable.

The criteria of judgment for dealing with the preceding case are as follows:

##### a) In the case of data measured twice

When  $R$  is below 30% of the average of two measurements, take the average value.

When  $R$  is equal or above 30% of the average of two measurements, repeat the measurement.

(where  $R$  is the difference of two data)

##### b) In the case of data measured once

Seek the average ( $\bar{X}$ ) and standard deviation ( $\sigma_{n-1}$ ) from past ten measurements,

When the measurement data is below  $\bar{X} \pm 2\sigma_{n-1}$ , adopt it.

When the measurement data is equal or above  $\bar{X} \pm 2\sigma_{n-1}$ , repeat measurement.

There is a need to investigate and record any lapse in the gathering of data in order to prevent any recurrence of abnormal data.

#### (3) Recording of Measurement

It is necessary to record and keep the following information:

- adjustments, operation and readings of instruments and tools used for sampling;
- conditions of custody and treatment of sampling bottle;
- sample condition, sampling method, sampling point (location), sampling date;
- observations on the sample (Sediment: external appearance, odor, foreign matter in sample, depth of sampling point etc.);
- preparing condition of sample;
- operation and readings of analytical equipment; and
- recording of other important information (dilution ratio, sample volume etc.).

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### 3.2.5 Report for Accuracy Management

It is necessary to record the following information:

- standard operating procedure
- measuring result of detection limit,
- result of operation blank,
- sampling and pretreatment of samples,
- result of collection test after addition,
- sensitivity changes of measuring apparatus, and
- whole measuring process.

A series of accuracy control management activities from sampling to report making is shown in Figure 3.5.

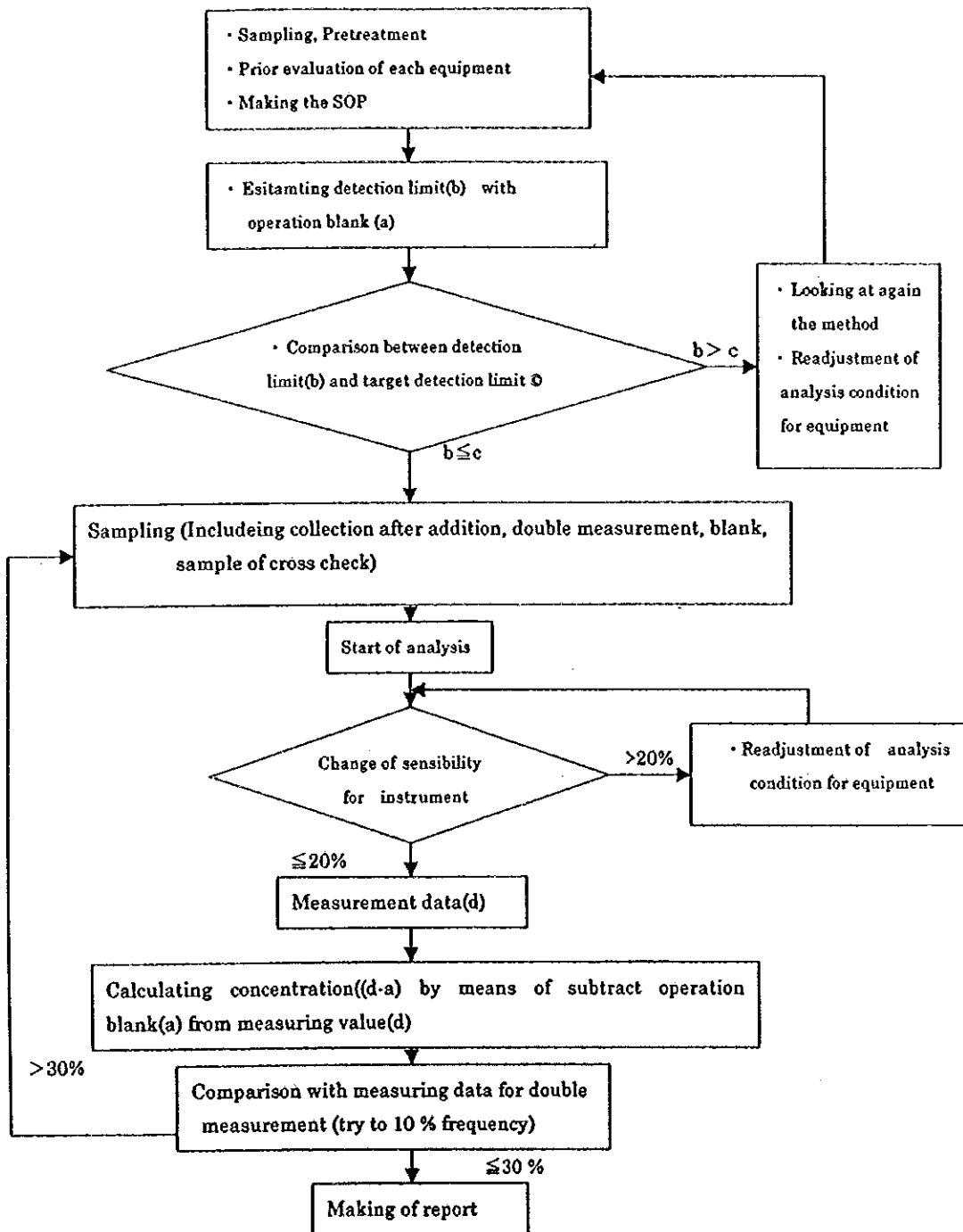


Figure 3.5 Flowchart of Accuracy Control Management

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### **3.3 Human Resource Development**

#### **(1) Necessary Skills for Coastal Water Quality Monitoring**

The activities of Coastal Water Quality Monitoring are divided into three: sampling, water quality and sediment analysis and data management. To properly undertake these activities, the following are required:

- water quality monitoring planning;
- appropriate water quality and sediment sampling;
- physical and chemical analysis; and
- data management.

Water quality sampling and data management require knowledge of coastal environment including physical, chemical and biological processes. Sampling activities should also consider coastal environmental conditions. Although modern chemical analyzers have black boxes, laboratory personnel should understand the principle of physical and chemical analysis. Since laboratory assistants also carry out laboratory work, they should have knowledge of basic skills. Quality control of laboratory work is also important since it could ensure reliability within and among laboratories.

Therefore, Coastal Quality Monitoring staff should develop the skills to handle the following concerns on coastal environment, including physical oceanography, chemical oceanography and biological oceanography:

- water quality,
- sampling for water quality,
- water quality analysis,
- sediment analysis, and
- statistics and quality control.

#### **(2) Approach to Human Resource Development**

Human resource development can be approached two ways: (1) on-the-job training, and (2) off-the-job training.

##### **a) On-the job-training**

Coastal Water Quality Monitoring staff are trained through daily work. For fieldwork, Regional Laboratories and Monitoring Site Offices could organize sampling teams, and members can learn from each other.

In the laboratory, analysts are assigned by shifting parameters. Newcomers initially

conduct simple analysis of parameters such as pH, DO, SS of water samples, and ignition loss and particle size of sediment samples. Next, they carry out analysis using a spectrophotometer, then an atomic absorption spectrophotometer or gas chromatograph. It is recommended that senior laboratory staff lead in the conduct of analysis of parameters so that others could observe and learn.

Table 3.4 Topics of Technical Seminar

Skills	Topics
Monitoring Planning	<ul style="list-style-type: none"> <li>• monitoring process</li> <li>• methodology of planning</li> <li>• data networking and integration</li> </ul>
Fieldwork	<ul style="list-style-type: none"> <li>• navigation</li> <li>• operation and maintenance of equipment</li> <li>• observation of hydrological conditions</li> <li>• sampling for water quality</li> <li>• sampling for hydrological conditions</li> </ul>
Water Quality Analysis	<ul style="list-style-type: none"> <li>• seawater quality analysis</li> <li>• sediment analysis</li> <li>• biological analysis</li> <li>• quality control</li> <li>• operation and maintenance of equipment</li> </ul>
Simulation Model	<ul style="list-style-type: none"> <li>• types of simulation models</li> <li>• practice of simulation</li> </ul>

b) Off-the-job training

Off-the-job training programs are not only for analysts but for assistants as well. The training programs should cover coastal environment, sampling methodology, and for the benefit of laboratory assistants, basic knowledge of chemical analysis.

The proposed Tampico Core Center for Coastal Water Quality Monitoring is one of the training centers for water quality monitoring. The Autonomous University of Baja California has marine science curricula. It is recommended that *CNA* contract the University to give lectures on coastal environment for *CNA* staff. Water quality and sediment analyses are almost the same as freshwater analysis so the technical seminars for chemical analysis could be held with the cooperation of *PROMMA*.

Recommended subjects for coastal water quality monitoring are shown in Table 3.4.



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c) Annual training schedule

It is recommended that the Laboratory Head prepare an annual training schedule well in advance in order to carry out a systematic education and training. For example:

- Common training; basic training (at the time of appointment) three years after appointment and upon promotion to a responsible position, etc.
- Special training; participation in a cooperative study with an outside researcher regarding a specific problem, or participation in a workshop and dispatch to some symposium.

It would be more effective if *CNA* were to design an integrated training program with the cooperation of concerned organizations.

d) Others

- The analytical laboratory may not be able to handle certain cases like pinpoint a new occurrence of environmental pollution or use a special equipment. In this case, an advanced education training system, such as cooperative research with a university, and the dispatch of analysts to research institutes abroad, should be established
- It is necessary to keep abreast of the times and to enhance skills in order to cope with the rapid pace of technological advancements and the increasing occurrence of environmental pollution. To this end, laboratory specialists could engage in research work in conjunction with some academic institutions. It would also be a great help to have a budget for technical books and subscriptions to academic journals and so on.

Table 3.5 A sample of Form-1 List of Facilities and Equipments

Form-1 List of Facilities and Equipments					
Item	Code No.	Detail of Facility			
		Brand	Model	Serial No.	Remark
<i>Electric analytical balance</i>	<i>101-05</i>	<i>Mettler</i>	<i>MT-5</i>	<i>115381552</i>	<i>2g 0.001mg</i>
<i>Apparatus for pure water</i>	<i>103-01</i>	<i>Organo</i>	<i>Osmoclear-PRP-100</i>	<i>214965A</i>	<i>reversed-osmotic/ionic exchange type</i>
<i>Spectrophotometer</i>	<i>201-01</i>	<i>Hitachi</i>	<i>U3000</i>	<i>04NB-001</i>	<i>190-900 nm</i>
<i>TOC analyzer</i>	<i>212-01</i>	<i>OI Corporation</i>	<i>MODEL 700</i>	<i>6307-153</i>	<i>Wet-oxidation-infrared type</i>
<i>pH meter</i>					
<i>Gas chromatograph</i>					
<i>Salinometer</i>					
<i>Refrigerator</i>					
<i>Electric furnace</i>					
<i>Centrifugal separator</i>					
<i>Autoclave</i>					
<i>Draft ventilation unit</i>					
<i>Ultrasonic washer</i>					
<i>Laboratory Table</i>					



Table 3.6 (2) A sample of Form-2 (2) Record of Malfunction and Repair

Form-2(2) Record of Malfunction and Repair

Facility or Equipment	:	
Brand	:	
Model	:	Serial No. :
Code No.	:	
Purchase Date	:	
Selling Agent	:	
Contact	:	
Tel and Fax	:	
Main Accessories	:	

Date of Repair	:	
Description of Malfunction:		
Description of Repair:		



Table 3.8 (1) Sample of Form-4 (1)

Regular Inspection Form of Facilities and Equipment

Form-4(1) Criteria for Regular Inspection Sheet for Facilities and Equipments

Name of Facility or Equipment : *Atomic Absorption Spectrometer*

Inspection Parts	Inspection Method	Inspection Criteria	Measure for Malfunction
<i>Appearance</i>	<i>Confirmation with eye</i>	<i>Stains and damages</i>	<i>Replacement or repair in the extreme cases</i>
<i>Light source</i>	<i>Confirmation with eye</i>	<i>lighting</i>	<i>Replacement of the lamp after confirmation of the life time of Lamp</i>
	<i>Operation</i>	<i>Set up the electric current</i>	<i>Replacement of the lamp after confirmation of the life time of Lamp</i>
<i>Optical system</i>	<i>Operation</i>	<i>Smooth movement of the slit</i>	<i>Repair if impossible to adjust</i>
	<i>Operation</i>	<i>Adjustment of the wave length</i>	<i>Repair if impossible to adjust</i>
<i>Cooling water</i>	<i>Confirmation with eye</i>	<i>Leak and clog</i>	<i>Replacement of the parts</i>
<i>Burner</i>	<i>Confirmation with eye</i>	<i>Stability of the fire feature</i>	<i>Cleaning of the slot</i>
	<i>Confirmation with eye listening</i>	<i>Smooth suction of the nebulizer</i>	<i>Removal of stains</i>
	<i>Operation Confirmation with eye</i>	<i>Adjustment of the stage Smooth discharge of the drain</i>	<i>Repair if impossible to adjust Removal of stains</i>
<i>Gas system</i>	<i>Confirmation with eye</i>	<i>Adjustment of it without leak</i>	<i>Replacement of the parts Repair if impossible to adjust</i>
	<i>Confirmation with eye</i>	<i>Pressure of the gas and flow rate</i>	<i>Repair if impossible to adjust</i>
<i>Compressor</i>	<i>Confirmation with eye</i>	<i>Functioning of the stopper, drain, lubricant, filter etc.</i>	<i>Replacement of the parts Repair if impossible to adjust</i>
<i>Recorder</i>	<i>Confirmation with eye</i>	<i>Precise movement</i>	<i>Repair if impossible to adjust</i>
<i>Accessories and expendables</i>	<i>Confirmation with eye</i>	<i>There are accessories and expendables</i>	<i>Purchase them as soon as possible if not.</i>
<i>Option</i>	<i>Confirmation with eye</i>	<i>Confirming existence of option parts</i>	<i>Purchase them if necessary</i>

Table 3.8 (2) A sample of Form-4 (2)

## Periodic Inspection Form of Facilities and Equipment

Form-4(2) Criteria for Periodic Inspection Sheet for Facilities and Equipments				
Name of Facility or Equipment: <i>Atomic Absorption Spectrometer</i>				
Inspection Items	Inspection Method	Frequency	Inspection Criteria	Measures for malfunction
	check			
1. Wave length of Indicator - Accuracy of indicated value - Reproducibility of indicated value	Confirm it with standard solution of Cu (2 mg/l) Confirm it with standard solution of Cu (2 mg/l)	6 Months	Within $\pm 1$ nm  Within $\pm 0.5$ nm	Ask the agent to inspect and repair it.
2. Reproducibility	Measure zero-correction solution and span-correction solution one after another three times, and to calculate deviation from the mean of the difference between two values.	6 Months	Within $\pm 3\%$ of whole scale	Ask the agent to inspect and repair it.
3. Stability Zero-drift (baseline drift)  Span-drift  Noise	Confirm it with stated zero-correction solution (prepared as 5 ml conc. $H_2SO_4$ is diluted with distilled water to 1000 ml) Confirm it with stated span-correction solution Confirm it with stated span-correction solution	6 Months	Below 0.01 absorbance in 3 minutes  Within 3% of the whole scale in 3 minutes Within $\pm 3\%$ of the whole scale	Ask the agent to inspect and repair it.
4. Response	Measure the time required for the 70% change (to adjust indication to absorbance 0 (or 100% transmittance) and to measure time since cut-off of light)	6 Months	within two seconds for the most rapidly response	Ask the agent to inspect and repair it.
5. Tolerance	Prepare calibration curve with zero -correction solution and span-correction solutions (Cd, Cu, Cr, and Pb) and to measure indication at a half of concentration of span-correction solution	6 Months	within $\pm 5\%$ of the whole scale	Ask the agent to inspect and repair it.

Table 3.8 (3) Sample of Form-4 (3)  
Maintenance and Inspection Form of Equipment

Form-4(3) Sheet for Maintenance and Inspection of Equipments

Date : \_\_\_\_\_

Name of facility or equipment : *Atomic Absorption Spectrometer*

Model and Code No. : *Shimazu AA-660 No.230-5*

Place : *3F*

Inspection Item		Criteria for check	Inspection time			Inspection Method	Measure For Malfunction	Exami- nation result
Object	Item		Daily	6 months	Mal- function			
Light source	Stain on window of light flux	no stain	O	O		Confirmation with eye	to wipe it off with clean and soft cloth	
	Lighting	to be able to light it	O	O		Confirmation with eye		
	Abnormal current		O	O			Replacement	
Whole optical System	Dry condition	not to be wet	O	O		confirmation with eye		
Mirror and lens	Stain	no stain		O		confirmation with eye		
Cell for mercury	Stain on window of light flux	to be able to operate	O	O		confirmation with eye		
	Stain on inner wall	no stain	O	O		Confirmation with eye		
Capture of Exhausted mercury vapor		to be able to completely capture mercury vapor	O	O		confirmation with eye		
Air flux of a pump	Adjustment	to be able to adjust it		O		to confirm under operating condition		
Position of cell	Adjustment	to be able to set it at optimal position		O		to confirm under operating condition		
Lamp	Current	to be able to adjust it to stated current		O		to confirm under operating condition		
Wavelength	Adjustment	to be able to adjust it to stated wavelength		O		to confirm under operating condition		
Zero Adjustment	Adjustment	to be able to adjust it to zero position		O		to confirm under operating condition		
Span Adjustment	Adjustment	to be able to adjust it to stated span position		O		to confirm under operating condition		
Stability	Zero drift			O		to confirm with stated zero-correction solution		
Reproducibility	Accuracy	deviation: within 3%		O				



Table 3.9 Sample of Form-5 Record of Operation of Facilities and Equipment

**Form- 5 Operation Record for Facilities and Equipments**

Name of Facility or Equipment : Spectrophotometer  
 Maker and Model :Hitachi U-2000  
 Serial No. :220-10  
 Code No. :0247-007

No.	Date	Starting time	Termination time	Functioning	Measure for malfunction	Operator
1				Function Failure		
2				Function Failure		
3				Function Failure		
4				Function Failure		
5				Function Failure		
6				Function Failure		
7				Function Failure		
8				Function Failure		
9				Function Failure		
10				Function Failure		
11				Function Failure		
12				Function Failure		
13				Function Failure		
14				Function Failure		
15				Function Failure		
16				Function Failure		

Item	Check Items	Criteria for Check	Method of Check	Measure
Lamp	Lighting	To be able to light it	Confirmation with eye	-
Chamber of sample	Stain and corrosion	Neither stain nor corrosion	Confirmation with eye	cleaning

note: At the finish of work on each weekend, the inside of sampling tube must be washed with rinse liquid, and the inside of sampling tube must be washed with pure water in order to eliminate rinse liquid at the beginning of work in the next week.

