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METEOROLOGY AND ENVIRONMENTAL
PROTECTION ADMINISTRATION (MEPA)

THE STUDY ON
AN ENVIRONMENTAL ASSESSMENT AND MONITORING OF ARABIAN GULF IN THE KINGDOM OF SAUDI ARABIA

SUPPORTING REPORT

Guidelines for Sea Water Monitoring along the Gulf Coast in KSA

January 2001

CHIYODA-DAMES & MOORE CO., LTD.

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Guidelines for Sea Water Monitoring along the Gulf Coast in KSA

This guidelines are developed for sea water monitoring along the Gulf Coast Area of the kingdom of Saudi Arabia based on the Investigation Study implemented by MEPA and JICA during the period from February 1999 to August 2000.

1. Introduction

Marine monitoring programs that attempt to detect human environmental impacts will fail if they are poorly designed, because illogical sampling designs produce results that are impossible to interpret with scientific certainty.

Comments

Typical problems preventing the collection of valid data and useful results include:

- lack of clear-cut questions, hypotheses and tests about the possible causes and effects of the monitored activities or variables;
- poor recognition or understanding of the natural processes, events and/or human activities which influence the variables being monitored;
- inadequate controls or baselines (= 'background sampling');
- insufficient replicate sampling over distance, time and measurement, all of which prevent meaningful interpretation of monitoring program outputs because of:

  (a) lack of data showing the actual 'real-world' variations due to natural changes and events over time and space; and/or

  (b) no results showing the size of the errors arising from the sampling and measurement methods.
- Inappropriate statistical testing (and/or insufficient of statistical 'power') to detect with certainty the occurrence of an impact and/or its true cause.

Poorly designed monitoring programs prevent valid interpretation and use of data from the subsequent (and often expensive) laboratory analyses.

Without clear-cut, logical and statistically sound sampling designs, monitoring to detect human impacts and provide information for marine management actions will be ineffective and inefficient.

2. Objectives

This guidelines are developed for sea water quality monitoring along the Gulf Coast Area in the Kingdom of Saudi Arabia to maintain the monitoring technology in high level.

Comments

2.1 Purposes of Marine Monitoring Programs

Coastal water quality monitoring can be undertaken for many different purposes.
The USNRC (1990) gives two very useful definitions of marine monitoring. These are:

(i) ***"a program of modelling, repeated measurements, analysis and information synthesis that predicts and quantifies environmental conditions or contaminants, and incorporates that information effectively into decision-making in environmental management". Therefore...***

(ii) ***"...marine monitoring is simply the sensory component of marine environmental management".***

Both definitions recognise that marine monitoring activities cover a wide range of purposes and objectives. More importantly, both emphasise that monitoring programs should never be established without clear reference to environmental management policies, strategies and goals. The ultimate purpose of all monitoring programs is therefore to facilitate the management and protection of important coastal resources and beneficial uses.

Most marine monitoring programs represent one of three main types:

- Regional monitoring programs
- Specific monitoring programs
- Highly-focussed programs

Regional monitoring programs are usually undertaken to monitor the 'health' of marine environments. For example, to detect any unacceptable degradation to coastal water quality and regionally-important marine habitats such as seagrass beds, mangroves and coral reefs. Regional monitoring programs are considered a fundamental requirement of sustainable development (e.g. Clarke et al, 1991). Regional monitoring programs may have broad objectives, with the monitoring activities defined as *"repetitive data collection for the purpose of determining trends in the parameters monitored"* (e.g. Chapman et al, 1987).

If regional data is not collected, it is not possible:

(a) to understand broad-scale changes with respect to natural processes and human activities;

(b) to identify potential problems before they become critical.

Specific monitoring programs are undertaken for narrower objectives. For example, to check if existing environmental protection measures and procedures used by a factory or utility (such as the location, design and discharge contents of its coastal outfall) are (1) operating in the correct manner, and (2) are sufficient to prevent degradation of local coastal water quality and habitats.

Highly-focussed monitoring programs are highly quantitative, and may be implemented to demonstrate if a predicted impact has occurred, using the ***statistical null hypothesis*** to achieve a ***high degree of scientific certainty***. Designing this type of program requires very careful planning, including use of a pilot program, to ensure its very specific objective/s can be achieved without impractically high costs and unobtainable funding needs. In particular, great care must be taken when:

(i) selecting a realistic the *null* and *alternative* (impact) hypothesis for the statistical test/s;

(ii) identifying the best indicators/parameters that can unequivocally (without argument) show if the impact has actually occurred;

(iii) choosing the best of these indicators to be used by the field monitoring team (i.e. those that can be practically and inexpensively sampled, measured and analysed); and

(iv) ensuring there are a sufficient number of sites and site replicates to overcome the problems of natural spatial-temporal variations and measurement errors (= provide sufficient *statistical power* to allow the hypothesis to be tested with a high level of *statistical significance* (at least 80% and often 95% confidence is required, particularly for cases that may involve legal proceedings).

Whichever purpose is selected for MEPA's future monitoring programs, it needs to be based on a **clear rationale** and sound, achievable **monitoring objectives.** Otherwise, it will be impossible to decide which, where and when particular indicators and parameters should be monitored to ensure the program is cost-efficient and provides useful and timely information.

2.2 Monitoring Objectives

To decide on the management priorities, direction and purpose of monitoring plan, it is useful to review the typical coastal protection objectives used by government agencies around the world.
The most common monitoring objectives are:

Regional Monitoring Objective: to determine trends in coastal water quality over time and geographic space. The purpose of this objective is to detect feared or unexpected long term deterioration resulting from the consequences of human activities, and before it is too late to prevent unacceptable impacts to water quality, marine habitats and their associated fishery and recreational resources. It differs from 'surveillance monitoring'[1] by focussing purely on water quality and sediment quality.

Compliance Monitoring Objective: For example, to confirm if a discharge or other activity by a factory, utility or municipality is being operated and managed in accordance with regulations and/or specific licence conditions.

Performance Monitoring Objective: For example, to determine if the environmental protection measures set by government regulation and/or licence conditions (such as the location, design, discharge rate and discharge contents of a particular coastal outfall) are sufficient for preventing unwanted degradation of local water quality and habitats.

Validation/Verification Objectives: these are highly focussed objectives used when there is a need to check a particular assumption, prediction, fear or an alternative option. Examples include:

(i) improving and confirming the capability of selected laboratory procedures and methods to achieve required detection limits;

(ii) confirming that certain contaminants or effects from a licensed discharge or other activity will not cause an unacceptable impact;

(iii) using pilot studies to check size, adequacy and cost of future replicate sampling designs;

(iv) obtaining a better understanding a local or regional coastal process that affects the fate of particular discharged contaminant/s;

(v) determining the capability of the region to receive, assimilate and disperse particular types of contaminants (e.g. biostimulants such as nitrates, ammonia or phosphorous);

(vi) evaluating alternative discharge locations and options;

2.3 Importance of monitoring activity in the Gulf

The coastal zone of the KSA Gulf region contains salt marshes (sabkahs), linear sand beaches and seagrass beds, with coral present on both inshore and offshore reefal areas. Significant marine coastal wildlife with high national and international conservation values includes many sea birds, sea turtles and dugongs.

Also, the Gulf Coastal Zone also provides KSA with significant recreational, fishery, drinking and industrial water resources. The need for clean sea water to maintain energy-efficient and cost-efficient desalination cannot be overlooked, as the coastal waters provide the main feed stock of the Kingdom's water supply for domestic, industrial and agricultural consumption.

The Gulf coastal waters and marine resource they support are both very vulnerable to the effects of contaminant and nutrient inputs.

On the other hand, it is becoming increasingly clear that, unless prompt regional and national management systems and countermeasures are introduced to reduce the number and size of chronic (long term) land-based sources of pollutants and bio-stimulants (especially nitrogen and phosphorous), water quality will continue to degrade. Degradation will eventually lead to wider-scale public health issues, further loss of fish nursery habitats, fishery stock damage, wildlife mortalities and economic losses to industry. Therefore the importance of ensuring there is an adequate and well-coordinated approach to the environmental management and monitoring of the Gulf Coastal Zones cannot be over-emphasised.

3. Planning

There are several items to be considered in the detailed planning of sea water quality monitoring programme, for examples;

i) Which contaminants are to be measured?
ii) Where are the samples to be collected?
iii) When is sampling to be done and how frequently?
iv) How many specimens (of what size) are to be taken for each sample?
v) Which tissue(s) are to be taken for analysis?

Comments

The head investigator, field biologist, analytical chemist, and statistician must consider each question during detailed designing and planning of the monitoring programme (e.g. prepare sampling instruction, estimate workload, prepare the necessary instruction sheets for the field staff, develop safeguards to ensure sample integrity, develop analytical quality control needs and data handling methods). All participants in the study must be fully trained in their role within the programme and recognize how their efforts unite with those of the other participants. The investigator must:

1) Design a sampling programme: select sufficient number of specimens with the required attribute; define sample site; specify sampling frequency and period; and design sample handling methods. This is based on the results of the pilot study and any other relevant information. A statistically sound base is required for sample design. Once the sampling programme design is completed, instruction sheet (sampling instruction) must be issued to field staff. Training is probably required at this point to ensure consistent sample collection and handling.

2) See that samples are collected, stored, and transported in way that ensures sample integrity (i.e. sample continuity, no loss and gain of contaminants before analysis). Again it will be necessary to prepare instruction sheets for field and laboratory staff.

3) Arrange for sample processing and storage and arrange for sample analysis by methods with the required accuracy, precision, and lower limits of detection. Collaboration between the head investigator and all participants is essential for success.

4) Ensure that there is a proper documentation system for tracing (tracking) samples from sampling to final data recording. The investigator must make sure that all team members are aware of, and comply with, the documentation system.

In general, to implement the actual monitoring work correctly and smoothly, the list of equipment the work plans for both field monitoring and laboratory analysis shall be prepared.

Comments

3.1 Preparation for Field Monitoring

Following preparation shall be necessary for sea water monitoring act.

3.1.1 Equipment List

It is the responsibility of the field work team to prepare their equipment prior to the sampling cruise. The equipment list for water sampling is provided in Table 3-1.

3.1.2 Multi-probe meter

Pre-cruise preparation and calibration of the Multi-probe meter (for pH, temperature, salinity, DO sand turbidity) takes place at least three days prior to the start of a cruise. Refer to the operators manual for a full description of calibration and maintenance procedures. Check the following items for inspecting the Multi-probe meter:

- Visually inspect the Multi-probe meter for abnormal wear or corrosion. Check to ensure that the deployment line is secure and that there are no abrasions. Make sure all fittings are secure and all fasteners are firmly in place.
- Verify that the communication connector is secure, waterproof and lubricated with silicone grease.
- Verify that the Multi-probe meter communicates correctly with the data terminal by running the terminal emulation program.
- Check the Multi-probe meter battery status and replace main batteries if voltage is below 6.0 volts.
- Calibrate the dissolved oxygen (DO), salinity and turbidity sensor on the base of the maintenance manual of the Multi-probe meter.

Table 3-1 Example of Field Monitoring eqipment List (1)

Equipment	Specification	Q'ty
Sampling Equipment		
Water sampler (Van Dorn 6 litre)	rubber band closing type, 6 litter	1
Water sampler (Van Dorn 10 litre)	rubber band closing type, 10 litter	1
Messengers for water samplers	chrome-brass	3
Eckman grab sediment sampler	chrome plated; 0.04 m^2 gape	1
Van Veen grab sediment sampler	stainless steel; 0.12 m^2 gape	1
Soil samplers	polycarbonate tube corer + cap	10
Plankton netS	NXX-13 mesh size	2
Sampling buckets and bins	Assorted, 40 litre	4
Assorted ropes	50 m, 25 m, 15 m	4
Stainless scoops and sterile spatulas	Assorted pkts	6
Stainless Trays	Various	4
Plastic Trays	Various	2
Shackles	stainless steel	4
Cable Ties	Narrow	100
Field Instruments		
Water current meter	electromagnetic, 0 - 250 cm/s	1
Hydrolab portable multi-probe meter	Temp, pH, DO, cond/salinity, turbidity	1
Portable ORP meter	Redox measurement	1
Secchi plate	dia. 30cm white plate, rope 30m	2
Sounding lead	3.2 kg, rope 30m	1
Pocket colorimeter for Residual chlorine	Electronic with powders	1
Glass Thermometer	0-50 °C	2
Portable GPS	Battery powered non-DGPS	2
KVH Datascope	Compass and range finder	1
Wind Speedometer	Silva pocket type	2
Preservatives and Containers		
Crushed water ice	20 kg	
Whirl Pak sterile polythene bags	L (15x23cm) : 13 (Yellow), 13 (White)	26
	M (11x23cm) : 21 (Yellow)	21
	S (7.5x18.5cm) :55 (White)	55
Ziploc resealing bags	L (22x33cm) : 10	10
	M (12x22.5cm) : 15	15
Cooler Boxes (55 litre & 120 litre)	Assorted sizes	5
Formalin	1 litre bottle of 10% Solution	1

Table 3-1 Example of Field Monitoring eqipment List (2)

Equipment	Specification	Q'ty
Field Record Items		
Field Record and COC Sheets	Printed White paper - assorted forms	30
Canon land camera with films	Films 36 x 10 packs	1
Disposable underwater cameras	Plastic type	3
Waterproof Labels	Assorted	50
Diver's board with pens	Magnetic self-cleaning	1
Waterproof marker pens, pencils and tape	Various	20
Miscellaneous		
Adhesive Tapes	Various	5
Razor blades	Packets of ss blades	2
Trash bags	Various	10
Disposable sterile polyethylene gloves	Box of latex disposable type	1
Kimwipes	Box	2
Replacement batteries	Various	10
Small hand tools	Packet of various hand tools	1
Distilled water in wash bottle	Various sizes	3
Diving, Health & Safety Equipment		
Spray jackets, hats, sun glasses	personal items	4
Protective cotton gloves	packet	10
Field First Aid Kit		1
Sunprotection lotion	bottles	3
Fins, snorkel and masks	personal sets	2

3.1.3 Water Sampler (van Dorn type)

The van Dorn type sampler, usually consists of a PVC cylinder and top and bottom caps. The top and bottom caps are hold open by a clamp against the tension of spring or a rubber connecting them through the bottle.

The action of a messenger releases the clamp, and the caps are pulled into position, closing off the top and bottom of the bottle. When the bottles are used in a series, the closure of one bottle released a messenger below it which travels down the wire and trips the next bottle. The samplers which are lowered to depths with both caps open are adequately flushed during the lowering.

3.1.4 Sediment Sampler (Van veen/Eckman type)

Grab sampling techniques are used for collecting sediments from surface and near surface sediments. In grab operations, a slow approach to the sea floor should be ensured to avoid the creation of "bow

wave" that disturbs the sediment-water interface prior to sampling.

Undisturbed surface sediment samples can provide an immediate assessment of the present levels of contamination in the area in relation to the textural and geochemical characteristics of the sediment. The sampler used must consistently collect relatively undisturbed samples to a required depth below the sediment surface and of sufficient volume to permit subsequent analysis.

Tightly closing grab samplers, of which there are many designs are usually adequate for studies of the most recently deposited layer. The 0.1 m2 Van Veen grab is recommended simply as an inexpensive, reliable and effective type sampler for sediments. Other samplers such as Ekman grabs are very efficient too to obtain relatively undisturbed samples of sediment.

3.1.5 Sampling Containers

The water sample containers required for each analysis parameter are listed in Table 3-2.

Table 3-2 Sampling Container List

Analysis Parameter	Container	Volume (ml)
Total Suspended Solid	Plastic	1000
Residual Chlorine	Plastic	1000
COD/TOC, Ammonia, Total Kjeldahl Nitrogen, Totoal Phosphorus	Plastic	2000
Cyanogen	Plastic	500
Metals	Plastic	500
Phenols	Glass	500
Oil & Grease, TPH	Glass	1000
BTEX (Benzene, Toluene, Ethylbenzen, Xylene)	Glass with teflon liner cap	250
Chlorophyll	Plastic	1000
Total Coliform	Plastic (sterlized)	100

The sediment sample containers required for each analysis parameter are listed in Table 3-3.

Table 3-3

Analysis Parameter	Container	Volume (ml)
Ignition Loss, TOC, Metals	Glass (wide mouth)	500
TPH, BTEX	Whirl pack	250

Each container is given a permanent sample label written in waterproof ink. At a minimum, each sample label includes station name and code, sample date, collection time, analysis required, and collector's initials.

Sample containers are cleaned and prepared by the laboratory prior to the start of a cruise. Sample containers are pre-labeled and packed into pre-cleaned Igloo coolers. A container list is prepared before a cruise starts and is used to verify that all samples are properly collected in the field. At least two personnel verify that the proper sample containers for each station have been filled with sediment and that the labels correspond to the proper station name and code.

3. 2 Work Plan for Field Sampling

The Work Plan for Field Sampling shall refer following.

3.2.1 Team structure

A team should be organized suited for the sampling program.
Normally, a team of,

- one cruise leader,
- one or two specialists (to take the special samples such as for plankton etc. , and to carry out in-situ measurements),
- one to act as bottle hanger plus one seaman as bottle carrier should be adequate.

In case that MEPA possesses their own vessel, following members are required additionally.

- one vessel captain,
- one or two seaman (to assist the vessel captain),

It is desirable that there should be as few changes as possible in the team and that a rigid routine should be insisted upon as to who does what. Besides overall supervision, the following duties are crucial and must be carried out or closely supervised by a cruise leader:

- final checking of samplers after clamping on rope;
- drawing water samples; and

It is highly important that the task of sampling should be approached in a calm and deliberate manner and that those concerned should have a proper amount of rest between stations.

3.2.2 Health & Safety

The vessel captain and/or the cruise captain is responsible for overseeing the safety of the vessel and crew while they are onboard the vessel. It is the responsibility of each crewmember to follow

common safety practices while performing their duties. General safety procedures used on the cruise involve (but are not limited to) the following guidelines:

H&S Supplies:

- Emergency Radio/Mobile Phone (on vessel)
- First Aid Kit
- 1 bottle of vinegar (for jellyfish stings)
- Two torches
- +15 Sunscreen Lotion
- Cooler box with ice, bottle water and cool drinks (1-2 L /person/day)
- Lunch boxes

Vessel Work Safety Meeting:

A "Vessel Work Safety Meeting" will be held prior to departure. This will include the following:

- Familiarise main features of vessel.
- Confirm emergency communication & transport system for serious injury or illness.
- Confirm location and type of Vessel Emergency Equipment for crew and workers. (how to find and use life jackets, flares, fire extinguishers, radio, etc).
- Confirm Vessel Emergency Plans for 'Man Overboard', Fire and Collision/Sinking.
- Team to show the crew the various work procedures that may happen at each site.
- Crew to show preferred Entry and Exit points for boat.

Anchoring and Engine/propeller 'switch off' routine when workers are in water.

Confirm no fishing by crew when snorkellers are in the water.

Potential Injuries and Precautionary Measures

Potential Injury/Risk	Precaution
Sun burn	Maximise shade use; use sunscreen cream regularly.
Heat exhaustion	Drink water regularly, and take more salt than your usual amount during meals.
Heat stroke	Work slowly; do not ignore early symptoms (dazzling light, dizziness, headache, hot dry itchy skin)
Sea sickness	Avoid engine exhaust fumes and small internal spaces; move away from bow (less motion); lie down; sip water and eat simple food between sickness; take 1-2 tablets at least 1 hour before start.
Rocking boat	Move carefully; wear boat shoes.
Cuts and abrasions	Use First Aid Kit promptly to clean skin cuts.
Rough weather/man overboard	Stop work and wear life jacket if sea very rough.
Boat fire or sinking	Follow Boat Drill.

Personal Protective Clothing:

- Hat with brim
- Sunglasses
- Loose long sleeve shirt
- Shorts and trousers
- Boat shoes

Note: Cotton clothing is much preferable to nylon or other artificial fibre

Snorkelling Inspections:

Minimum dress: T-shirt, shorts, socks, mask, snorkel, fins, diving knife.

Preferred: Booties, long cotton trousers or stinger suit, gloves.

Protocol:

- Engine switched off and ignition keys removed.
- Check anchor is holding the boat.
- Deploy 10 m safety line and float from stern of boat.
- Deploy a Diving Flag on boat.
- No fishing from boat when snorkellers are in the water.
- No more than two snorkellers in the water at one time.
- Always 1 look-out on deck with no other job to distract.
- Rescue snorkeller will always be on stand-by, with his mask, fins and snorkel located at convenient place near exit point.
- Snorkellers always to remain in visual contact with each other and the boat.
- Snorkeller to have rope to boat if visibility is less than 1 m.
- Emergency visual, audible and rope 'Recall to boat' and 'Help Me' signals to be confirmed, prior to entry into water.
- Do not touch corals or fish.
- Be wary of jelly fish.

3.2.3 General Paremeter Measurement

1) Air temperature

Air temperature is normally measured at sea at the height of the bridge. A thermometer is the useful instrument for monitoring variations in air temperature. The most common type of thermometer is liquid-in-glass tube attached to a graduated scal. The liquid is alcohol (which freeze at -117℃ or -179 · F). As the air warms, the liquid expands and rises in the glass tube; as the air cools, the liquid contracts and drops in the tube.

2) Wind

Wind speed

A cup anemometer is usually used to provide an accurate measurement of horizontal wind speed. The wind spins the cups (usually 3 or 4), thus generating a weak electric count, which is calibrated on a dial in meters par second, kilometers per hour, miles per hour, or knots. Several other types of anemometer are available, including the very sensitive hotwire anemometere. In this instrument, the wind blows past a heated wire, or wires, and the heat lost to the air is then caliblated in terms of wind speed. A cup of anemometer is recommended to use in this study.

Note: One knot = 1 nautical mile (1.85 km) per hour; 1 knot = 0.51 meters per second; 1 mile per hour = 0.44 meters per second.

Wind Direction

Wind direcrion is always designated as the direction from which the wind blows. For example, a wind blowing from the east toward the west is described as an " east wind", and a wind blowing from the northwest toward the southwest is a "northwest" wind. Measured clockwise from true north, an east wind is specified as 90 degrees, a south wind as 180 degrees, a west wind as 270 degrees, and a north wind as 360 degrees. The wind is recorded as 0 degrees only under calm conditions.

Wind direction should be measured by anemometer when the vessel is stationary. If it is measured when the vessel is moving, corrections have to be made according to the relative speed of the vessel and its relative direction with respect to the wind.

3) Cloudness

Observation of cloud cover is carried out by non-instrumental methods. Therefore, it is dependent upon the personal judgement of the observer. To acquire the required experience and comparability of data, the following procedure is recommended:

In making the observations it is necessary to stand in a position affording an uninterrupted view of the whole ski. It is recommended that one of the members of each sampling team be trained by a meteorologist. It is convenient to imagine the sky divided into quadrants by two drawn at right angles through the zenith. Each quadrant represents two-eight of the total sky.

4) Wave

Wave Direction

Wave direction means the direction from which the waves come. This is easily obtained either by signing directly across the wave front or by sighting along the crests of the waves and remembering that the required direction differs from this by 90 degrees. Direction is always recorded true, not magnetic.

Wave Height

The measurement of wave height is strictly based on estimations. The procedure to be adopted dependent on the length of the waves relative to the length of the ship. If the length of the wave is short in comparison with the ship's length, the height should be estimated from the appearance of the waves.

5) Water Current

Water current is measured by the Electro-Magnetic Current Meter which is composed of a Sensor Sonde with a Cable connected and a Display Unit. This is an oceanographic instrument enabling the real-time monitoring of the measured current speed and direction data.

Additional back up meters should be prepared along with spare parks kit. The station should be carefully selected considering various factors: security of the mooring, shipping traffic, local fishing activities, bottom material, etc.

Detailed instruction on handling, operation procedure and mooring are in the manufacture's manual. The instrument should be calibrated prior to deployment. Usually new meters are calibrated in the factory and should not need further calibration unless they are damaged.

6) Sea Surface Observation

Valuable information concerning oil pollution distribution patterns and seasonal trends may be obtained through a programme of regular reporting of oil slicks and other floating pollutants.

Whenever floating oil, petroleum residues or oil slicks, and other floating pollutants (plastics, rubbish, etc..) are sighted, they should be reported on the field record sheet. It is equally important to record the observation period during which no oil is sighted. Observation made from offshore structure such as oil rigs, pumping platforms, etc. should be reported once 24 hours. The observation method does not require any special instruments or equipment although a good pair of polarizing sunglasses may help to distinguish petroleum derived slicks from natural films. In addition, a lightweight pair of binoculars are also useful for observing slicks at distance.

3.2.4 General Water Quality Measurements

Water quality measurement methods at field are shown in Table 3-1.

Table 3-1

Parameters	Measurement Methods
Water color	Observation with naked eyes
Odor	Performed by personnel sense of smell
pH	Portable multi-probe meter
DO	Portable multi-probe meter
Chlorine	Portable Chlorine meter
Temperature	Thermometer or Portable multi-probe meter
Salinity	Portable multi-probe meter
Water clarity	Secchi plate
Water depth	Sounding lead

3.2.5 Sampling

3.2.5.1 Water Sampling

1) Sampling Routine

The following is a summary of the sequence of events before, during and after a typical station.

Preparation

a) Fix the site locations by using a portable GPS unit.

b) When captain gives permission, lower weight below surface.

c) Arrange water sampling in order of bottom and mid-depth.

d) Prepare sample bottles.

e) Measure and record general water quality.

f) Prepare all deck personnel responsible for sampling etc.

On Station

a) Water samples are collected using a van Dorn sampler or clean plastic buckets.

b) Check the rope connected firmly with the Sampler, when using van Dorn sampler.

c) Samples are poured into labeled bottles with added preservatives when required.

d) Samples are transported into cooler boxes maintained at 4°C. Preservatives and holding times for each parameter are shown in Table 3-2.

Table 3-2 Preservatives and holding times for each parameter

Analysis Parameter	Preservation	Holding Time
Total Suspended Solid	Cool, 4°C	48hrs
Residual Chlorine	Cool, 4°C	Immediately
COD/TOC, Ammonia, Total Kjeldahl Nitrogen, Totoal Phosphorus	Cool, 4°C	48hrs
Cyanogen	Cool, 4°C add NaOH, pH>12	14days
Metals	add HNO3, pH<2	28days (Hg) 6months (otheres)
Phenols	Cool, 4°C add HCl, pH<2	28days
Oil & Grease, TPH	Cool, 4°C	28days
BTEX (Benzene, Toluene, Ethylbenzen, Xylene)	Cool, 4°C add HCl, pH<2	14days
Chlorophyll	Cool, 4°C	Immediately to filtrate 28days (Frozen)
Total Coliform	Cool, 4°C	24hrs

Post Sampling

a) Verify that all samples are properly filled in the field by using the container list.

b) Verify that the labels correspond to the proper station name and code.

c) Rinse all of equipment in freshwater.

d) Reorganize equipment for safety while cruise.

2) Water Sampling Methods

Water samples are collected using a Van Dorn Type water sampler or clean plastic buckets, depending on location and depth. Samples are poured into labelled bottles with added preservatives where required, and these are stored and transported in cooler boxes maintained at 4°C with crushed ice. The samples are transported to the laboratory to arrive within acceptable holding time limits.

3) Handling of Samples

Samples are maintained on board the vessel and transferred to the laboratory. The field manager(s) are responsible for maintaining sample integrity throughout the cruise. Sample contamination is avoided by double bagging the sample containers, handling the containers with clean gloves, and

transferring the samples into sealed buckets/coolers immediately after sampling.

The samples that are held on crush ice are checked periodically to ensure that samples are appropriately protected and stored ice is added as required. Additionally, coolers containing wet ice are drained periodically to remove water from melted ice.

A field record is maintained for each site. The example of a field record is shown in Table 3-3. is signed by field personnel and water samples are shipped by field member people in coolers on enough crush.

4) Shipping

Chain-of-Custody (COC) procedures are used to document sample possession and integrity from the time of sampling until delivery and receipt by the laboratory.

COC is signed by field personnel and water samples are shipped by field member in coolers on enough crush. The objectives of COC are describes below and the example of COC form is shown in Table 3-4.

*Procedures should be established that ensure that samples are properly collected and preserved from the time the samples are collected until the corresponding data are submitted.

*A system for assuring positive identification of samples and documentation of all samples must be operational. To ensure sample integrity, chain-of-custody procedures including procedures for sample identification, sample receiving, and sample tracking, should be developed and instituted.

*Sample Identification

- To assure traceability of samples while in possession, there should be specified method for maintaining identification of samples in the field and throughout the laboratory.
- Each sample and sample preparation container should be labeled with a unique identifier that is cross-referenced with the corresponding documentation.

*Sample Receiving

- A sample custodian (and an alternate) responsibile for receiving all samples should be designated.
- The condition of the shipping and sample containers should be inspected and documented upon receipt by the sample custodian or his/her representative.
- The sample custodian or his/her representative should sign and date all forms accompanying the samples at the time of sample receipt.

*Sample Tracking

- Records documenting all phases of sample handling from collection to final analysis should be maintained.

Table 3-3 Example of Field Record Sheet

Samplers name :

Site No.: **Location:**

GPS, DOP :	Latitude (N) :	Longitude (E) :

Date		Time	

Weather Condition

Weather		Temperature (°C)		Cloudiness	
Wind Direction		Wind Speed (m/s)		Wave height	

Water Condition

Tide		Depth (m)	
Current Direction		Current Speed (m/s)	

Water Quality

Temperature (°C)		Water Color	
Salinity		Odor	
pH		Sheen	
DO (mg/l)		Rubbish	
Turbidity (NTU)		Res. Cl (as Total)	
Water Clarity (m)			

Sediment Quality

Sediment Color		Temperature (oC)	
Odor		ORP (mv)	
Texture			

Observations and Comments

Table 3-4 Chain-of-Custody Sheet (Water Samples)

No. Page : of

Date Sampled:

Sampler:

Remarks:

No.	Sample ID	Time Sampled	Type of Sample	Bottle Type	Volume (ml)	Q'ty	Analysis Parameter																				Notes

Supplied to Laboratory by : (Name) _____

(Signature) _____

(Date/Time) _____

Received at Laboratory by : (Name) _____

(Signature) _____

(Date/Time) _____

Table 3-4 Example of Chain-of-Custody Sheet (Sediment/Soil and Biota Samples)

No. Page : of

Date Sampled:

Sampler:

Remarks:

No.	Sample ID	Time Sampled	Type of Sample	Bottle Type	Volume (mL)	Q'ty	Particle Size	Ignition Loss	COD/TOC	Hg (Mercury)	As (Asenic)	Cr (Chromium)	V (Vanadium)	Other Metals (Cd,Co,Cu,Ni,Pb,Zn)	BTEX	TPH	PCBs	Plankton, Biota	Notes
			Sediment (SD), Soil (SL), Biota (B)	Glass (G), Plastic (P), Whirl pack (W)			Analysis Parameter												

Supplied to Laboratory by : (Name)

(Signature)

(Date/Time)

Received at Laboratory by : (Name)

(Signature)

(Date/Time)

3.2.5.2 Sediments Sampling

1) Sampling Routine

The actual collection procedure is quite simple :

a) Prepare all sample containers for sedimentological and chemical samples.

b) Clean the sediment grab thoroughly with hot soapy water, rinse with tap water. Avoid placing the grab sampler on the open deck, keep in a large plastic or aluminum tub while not in use.

c) Clean a large sized plastic tub.

d) Cook the grab sampler.

e) Haul sampler on-board.

f) Initially, a visual inspection should be made of the sample by means of the small trap doors on top of the grab to ensure that the sample has been collected in an undisturbed state and to determine if there is water on top of the sample. If water is present, it can be siphoned off with a glass tube or slowly drained so as not to wash the sample unduly.

g) Once the top of the sediment is exposed, visual estimates of grain-size (coarse, medium, fine grained), color, and the relative proportions of the components should be made and recorded. In-situ measurements such as ORP or pH can be made by inserting the appropriate electrodes into the sample.

h) Most fine grained sediments usually have a thin, dark yellowish brown surface layer resulting from the oxidization of iron compounds at the sediment-water interface. Since in most cases this layer represents the material being deposited at the present time, it should be sampled carefully with a non-contaminating utensil such as a plastic spatula for trace metal determination. Only cleaned plastic utensils should be used to collect sediment samples for trace metals determination, and cleaned stainless steel utensils for organic analyses.

i) After the surface layer has been sampled, the grab can be opened and an additional sample, representative of the subsurface, can be obtained. Observation of this material should include color and textural characteristics.

j) Store all sediment samples under refrigeration(4℃) until they are transported to the laboratory.

2) Sampling Methods

Subtidal sediment samples are obtained using a stainless steel Van Veen grab or by Ekman box grab, whilst intertidal sediments are obtained by using polycarbonate corer tubes.

Samples for sediment chemistry are always collected from the upper layer (0-5 cm surficial sediment layer). The collected sample is pooled and mixed in clean stainless trays and then sub-sampled to provide a series of composite sub-samples for each site. These are stored in sterile plastic Whirl-Pak bags, Ziplock bags and/or pre-cleaned glass jars depending on the analyses required. All sediment samples are stored and transported to the laboratory in cooler boxes maintained at 4°C by crushed ice.

Measurement methods for sediment samples at field are shown in Table 3-5.

Table 3-5

Parameters	Measurement Methods
Temperature	Portable probe meter
Color	Observation with naked eyes
Odor	Performed by personnel sense of smell
ORP (Oxidation Reduction Potential)	Portable probe meter

3) Handling of Samples

Samples are stored aboard the vessel according the type of analysis performed. Normally, samples are stored on crush ice.

The samples on crush ice should be checked periodically to ensure that samples are appropriately protected and ice should be added as required. Additionally, coolers containing wet ice should be drained periodically to remove melt water.

In addition to the ship's log, a field record is maintained for each site. The field record is same one shown in 3.5.1-3).

4) Shipping

see 3.5.1-4)

3.2.5.3 Plankton Sampling

1) Preparation for sampling

It is essential that samples be properly labeled. Information contained on the labels should be sufficient to identify the sample with certainty. The labels should be carefully fixed on the sample jar.

This label should contain the following information: name of ship, cruise number, date, time, station designation, depth of tow, gear used, mesh size, type of haul, duration of haul, collector's name and number of jars in the sample.

2) Sampling Method

Plankton samples are obtained by towing an NXX13 Kitahara plankton net (0.001 mm mesh size; 0.07m^2 mouth size area) vertically from the bottom to surface. The total towed distance is recorded

to estimate the filtered volume. The filtered volume is calculated by using the following formula:

$V=A*d*Sw$

where V = filtered volume;
A = area of plankton net mouth;
d = distance the net towed;
Sw = sea water filtering rate (82% for Kitahara Plankton Net).

3) Handling of Samples

Each sample obtained from standard net washing is placed in a labeled polyethylene bottle and immediately preserved with 10% buffered formalin. In addition to the net sampling, water-bottle sampling method is also undertaken, in which two litres (2L) of water are collected and topped up with formalin to achieve a 10% concentration for preservation.

4) Shipping

COC procedures (described in 3.5.1-4)) are also used for the plankton samples.

3.3 Work Plan for Laboratory Analysis

The Work Plan for Laboratory Analysis shall refer following.

3.3.1 Team Structure

Laboratory analysis team should be organized suited for the sampling program.
One of the simplest teams is composed of,

- a laboratory director,
- a QA/QC director and,
- several technicians.

Laboratory director is responsible for allover laboratory work and have to check all steps from sample accept to submission of analytical result, and have to let the all technicians observe Laboratory management standards. QA/QC director is in charge of checking quality accuracy management condition of analyzed data and adjust their data quality sufficient to compare with other organization's data. Technicians are responsible for their specializing analysis and make sure to achieve accurate result.

3.3.2 Health & Safety

In order to carry out the laboratory work s in health and safety, lab staff should keep the following rules:

Tidiness

- Keep the laboratory clean and tidy. Before starting lab work, wipe your bench and equipment that will be used.
- Cleaning must be done by lab technician or qualified person. Janitors under the supervision of lab manager or lab technician, however, can do regular cleaning of floor and table.
- Do not leave obstructions in the passages.
- Do not leave dirty apparatus around the sink.
- When a job is finished, wash used glassware and dispose chemicals properly or arrange to store all chemicals * other than those in standard reagent bottles * and leave your bench empty.
- When a job is finished, do not leave dirty apparatus in the laboratory.

Self-protections

- Wear laboratory coat or work wear in laboratory to avoid staining or eroding your skin or clothes. For the same reason, shoes are needed in laboratory to protect your toe.
- Wear eye protection devices, such as goggles or safety glasses, when there is the slightest risk of splashes or flying particles reaching the eyes.

- Safety gloves and fume cupboard should be used at the time of handling toxic/dangerous substances.
- In anticipation of chemical splashes on your body or in your eyes, you must know where to find and how to operate the emergency shower and eyewash.

Sulfuric Acid and other corrosive liquids

- During the period of diluting concentrated acid, remember always to pour the acid slowly into cold water well stirred in an open basin beaker. Never pour water into concentrated sulfuric acid.
- Do not store acids and similar materials on high shelves or in a hot place.
- Wear eye protection and the appropriate protective clothes.

Forethought

- Before you start a new experiment, ask yourself or lab manager whether it is exactly the same as one that you have done. If there is anything new, there must be possibilities to happen unexpected issue.
- Do not alter the details of an installation without very carefully thinking out what the possible consequences may be caused.
- Manager should give enough information and precautions prior to order of new experiment or work.

Spillage

- Mop up at once when water or chemicals are spilled on the bench or floor.
- If the spillage contains any chemicals, ask lab manager how to treat it.
- If mercury is spilt it must be removed immediately, since mercury escape as vapor easily.
- In case of the spillage of large quantities of sulfuric acid or organic solvent, special adsorbent or absorbent can be used. Ask manager for treatment.

Waste materials

- Do not pour into the sinks large volume of solvent, heavy metals and inflammable liquids.
- Refer the procedure of waste treatment.

Labels

- See that bottles containing reagents are clearly labeled.
- Keep the adequate labels on sample containers.

Glassware

- Examine all glassware for defects before carrying out any experiments and washing.
- Do not carry a glassware (bottles, flask, etc.) by the cap or neck, since it may slip or break off.
- Make sure that any vessel you are going to carry is clean on the outside and your hands are dry

and not oily.

- Do not rapidly heat or cool thick-walled or normal glass apparatus. They will crack under such treatment.

Electrical Circuit

- Ensure that all resistance, cables and terminal arrangements are capable of carrying the desired current without overheating.
- All switches, sockets and terminal connections must be made correctly and firmly.
- All high voltage electrical equipment should have good earth connections. The handling of such equipment should be avoided in wet conditions.
- When pull out the electrical plugs, do not pull the electrical cord, but plug itself.

Fume Chamber

- Do not carry out on the open bench experiments likely to result in the generation of poisonous or unpleasant vapor/fumes, but work in a fume chamber.
- Make sure that the ventilation system is in order before use.

Fire

- Each room should be provided with fire extinguishers.
- Know the locations of the fire extinguishers and how to operate them.
- Do not use water unless you know it is safe to do so, electricity turned off, no organic liquids involved, and no chemicals that react dangerously with water.

Notice

- All warning and danger notices should be posted appropriate locations.

Eating and Smoking

- Eating and smoking are strictly forbidden in laboratory.

First-aid

- When chemicals adhere to skin or reach eyes, wash with running water for at least 15 minutes. During washing, call the lab manager and get instructions.
- In any case of poisoning, summon first-aid and a doctor. Speedy action is essential in poisoning cases.
- In case of burn, cool the burned area with running water or ice chilled water for at least 15 minutes.

3.3.3 Laboratory Management

Followings are the Manual for Maintenance of Laboratory Analysis.

1) Application

This manual is applied to the maintenance of laboratory equipment.

2) Definition

Equipment: All equipment for laboratory measurement and testing

Laboratory manager: the person who has the all responsibility of laboratory work

3) Procedure

a) Equipment list

Laboratory manager (call "manager" in this manual) should prerare "equipment list".

In "equipment list" next items should be included.

- Name of equipment
- Model number
- Serial number
- Manufacturer
- Control number
- Installation date

When new equipment will be installed or present equipment will be scrapped, manager should revise "equipment list".

b) Daily maintenance

Manager should prepare "daily maintenance program" and "maintenance record" (from) for each equipment.

In "daily maintenance program" next items should be written.

Check items

Criterion

Manager should check the "maintenance record" periodically and confirm that maintenance is implemented properly.

c) Long term maintenance schedule

Manager should prepare "long term maintenance schedule" and "maintenance record" (from) for each equipment. And manager should prepare the maintenance procedure for each check item.

In "long term maintenance schedule" next items should be written.

- Check items
- Name of part(s) which is(are) required to exchange
- Part(s) number or model number
- Document number of maintenance procedure

Manager should check "maintenance record periodically and confirm that maintenance is implemented properly.

d) Repair

Manager should prepare "Repair record".

In "repaire record" next items should be included.

- Name of equipment
- Repaired date
- Symptoms of failure
- Detail content of repair
- Responsible person

Manager should confirm the content of repair and condition of fixed equipment, then give the approval of reuse of that equipment.

3.3.4 Analysis Methods

1) Water Sample Analysis

Analysis methods of water sample are summarized in Table 4-1 and more detailed procedures are attached in Appendix. The sample analysis methods should be reviewed and renewed regulatory.

2) Sediment Sample Analysis

Analysis methods of sediment sample are summarized in Table 4-1 and more detailed procedures are attached in Appendix. It is better to review and renew the methods regulatory.

3) Granulometry (Particle size analysis)

Granulometry is the classification of sediments into various grade sizes. The procedure commonly involves two steps (1) wet sieving of raw sediments on a graded series of metal sieves, to separate the coarser fracutations above 4 ϕ (0.062mm), and (2) a further separation of the fine grained fraction (fine than 4 ϕ) by repeated collection of particled setting in an aqueous solution (pipette or hydrometer). The sieves are arranged in the following order from top to bottom: 10, 14, 18, 25, 35, 45, 60, 80, 120, 170, 230 (US Standard sieve mesh #).

Table 4-1 List of Analysis Methods

	Analysis Item	Method	Code
Water Analysis			
1	Residual Chlorine	Titratmetric/DPD Colorimetric	4500-Cl G
3	TOC	TOC analyzer	5310 B
4	TSS	Gravimetric	2540 D
5	NH_3	Spectrophotometric	4500-NH_3 B,F
6	TKN	Spectrophotometric	4500-N_{org} B
7	Total Phosphorus	Spectrophotometric	EPA 365.3
8	Cyanogen	Spectrophotometric	EPA 335.2
9	Magnesium	AAS	3500-Mg B
10	Cd, Pb, Zn, Cu, Co, Ni	solvent extraction - AAS	3500 B
11	Chromium	solvent extraction - AAS	3500-Cr B
12	Mercury	vapor generator - AAS	3500-Hg B
13	Arsenic	hydride generator - AAS	3500-As B
14	Phenols	Spectrophotometric	EPA 420.1
15	Oil & Grease	Oil contents meter	EPA 413.2
16	TPH	solvent extraction - oil contents meter	EPA 418.1
17	BTEX	headspace - GC/FID	EPA 602
18	Chlorophyll	Spectrophotometric	10200 H
19	Total Coliform	membrane filtration	9222 B
Sediment Analysis			
21	Ignition Loss	Gravimetric	-
23	TOC	Titratmetric	Moopam IV.4
24	Cr, Cd, Pb, Zn, Cu, Co, Ni, V	acid decomposition - AAS	EPA 3050-B
25	Hg	acid decomposition - AAS	
26	As	acid decomposition - AAS	
27	TPH	solvent extraction - oil contents meter	5520 E,F
28	BTEX	headspace - GC/FID	EPA 5021

4) Plankton Counting and Analysis

Laboratory methods for plankton sample analysis consisted of measuring the settling volume, identifying the taxonomic groups, and counting of the number of identified plankton. Details of each method are summarized as follows:

a) Measurement of the settling volume

Water-bottle samples were transferred to a measuring cylinder and settled for 24 hours. The precipitate was then recorded as the proportional quantity of the total volume.

b) Taxonomic Identification of Plankton

Small (0.1ml) sub-samples were placed on glass microscope slides and placed under an optical microscope to permit identification of planktonic taxa at the level of order, family, genus or species, wherever possible. The relative abundance (proportional frequency) of each identified taxon was recorded semi-quantitatively using the following method.

+	rare	(appearance rate, <10%)
++	uncommon	(appearance rate, 20-30%)
+++	common	(appearance rate, 40-60%)
++++	frequent	(appearance rate, 70-80%)
+++++	abundant	(appearance rate, >90%)

c) Counting

Small sub-samples (0.1ml) were placed on 76×26 mm glass microscope slides with a 10 micron grid graticule, and examined under an optical microscope. The number of each plankton taxon was counted three times, and the total number of plankton per 1L of sample was calculated using the following formula:

$A=(a1+a2+a3)\times 10{,}000/3n$ where

A= number of units/ml

a1+a2+a3 = number of plankton counted by each trial (3)

n = concentration factor (= 1/dilution factor)

The results were used to calculate the Shannon-Weaver Diversity Index (D), which is as follows:

$$D = -\sum_{i=1}^{s} pi \log_2 pi$$

where

$pi = Ni / N$,

s= the number of species in a sample,

N= the number of individuals in a sample

Ni = the number of individuals of species i in a sample.

4. Data Analysis, Management and Reporting

* Can the proposed sampling effort meet the needs of the monitoring program as defined in the performance criteria associated with the stated objectives?
* How can the proposed program be modified to ensure that these objectives are met?

This is an iterative process to proposed sampling designs are evaluated and modified, if necessary, to meet the overall objectives. The tools for conducting these analyses are described below.

Comments

The overall Data Analysis performance of the monitoring program should be evaluated at periodic intervals. Initially, this evaluation should take place at the conclusion of the first year of sampling. This evaluation should compare the results with the expected monitoring performance, and a list of required modifications should be prepared. Opportunities for streamlining the program should be identified, and the performance criteria should be reviewed and revised, if necessary, for subsequent evaluations.

The primary tool for conducting these analyses is statistical power analysis. Statistical power analysis provides an evaluation of the ability to detect statistically significant differences in a measured monitoring variable. The importance of these analyses can be seen in the examination of the possible outcomes associated with testing the null hypothesis

Data Management

Data management and data analysis, two key components of the monitoring study that are often overlooked in the design of monitoring programs, are as important to the success of the monitoring effort as the collection and laboratory analysis of field data. Moreover, the cost of effective data management/data analysis can be substantial.

The development of a data management strategy must consider the following questions:

* Where will the data go?
* How will these data be stored?
* Who will maintain the data base?
* How will data be checked and loaded into the database?
* How accessible will the data be?
* Will statistical, graphical, and report generating tools be available?
* How much will it cost?

A computer system will be essential for the management of the data collected by the estuary monitoring programs. It should be operational prior to implementation of the monitoring program and should have the following attributes:

* Centralized storage of raw data
* Easy access and use
* System documentation
* Quality assurance procedures
* Linkage to graphical, statistical and report generation routines
* Long term availability and flexibility

The quality assurance information that must be reported with each data set must be defined prior to implementation of the monitoring effort. The objective is to identify key field, laboratory and quality assurance information that would allow future users of the data to make informed decisions regarding the comparability of historical data sets. This set of basic reporting requirements should be developed for all data types collected.

Reporting

Field data and laboratory analysis information should be entered into database (shown in Table 7-1). Followings are main items should be recorded in the database,

- Sample details (Site location, sampling time, etc),
- Tidal regime,
- Meteorological and ocean condition,
- Field parameters (water and sediment),
- Laboratory results (water, sediment and plankton),
- Other description.

Hardcopy records and source documents for both the cruise event data and the laboratory analysis data should be kept for a period of 5 years after the last day of the cruise.

5. Quality Assurance

In order to keep the accuracy and reliavility of the whole monitoring activity, the systematic quality assurance procedure shall be constructed.

5.1 General QA/QC Requirements

A QA program shall be developed and implemented with the participants' organization that is in accordance with the procedures and recommendations of this document. The purpose of this section is to define the recommendations of the participants' QA program.

5.2 Field Quality Assurance Procedures

1) Annual Calibration

*An annual calibration is an extensive and throughout calibration using standards or instruments to ensure the parameter precision.
*These calibrations will be performed on each instrument at least annually.

2) Calibration Check

*A calibration check is a verification performed before and after each cruise to ensure that the instrument response is comparable that which exist at the annual calibration.
*When the calibration check indicates a significant change during a cruise, the instrument should be recalibrated.

3) Check Sample

*A check sample is a water sample that is collected simultaneously with an in-situ measurement and returned to the laboratory for analysis.

5.3 Laboratory Quality assurance procedures

1) Method Blank

*A method blank is a volume of ASTM Type II reagent grade water this is carried through the entire analytical procedure. The purpose of a method blank is to determine the level of contamination associated with the processing and analysis of samples.

*A method blank should be analyzed once for every 10 samples (preferable), however every 20

samples is acceprable for those instances where the contaminations are low and this is the total sample number.

*If the concentration of analyte exceeds the MDL, laboratory or reagent contamination should be suspected. If the analyte concentration is 5 times the MDL or greater, then corrective action is required and reanalysis if possible.

2) Matrix Spike (not required for chlorophyll, PHOSP, PC and PN)

*A matrix spike is used primarily as a means of evaluation bias that may result from the analysis of a particular matrix when using the specific procedure. The saline, aqueous matrix has been demonstrated to impart bias in some analyses. Sampling spike analysis involves the introduction of a know amount of the analyte of interest into one of two aliquots from a well homogenized sample and a calculation of spike recovery.

*The spike concentration must be greater than the original or background concentration of the sample and not less than four times the calculated MDL.

*The sample is spiked prior to all steps in the analytical process, particularly when a digestion is involved.

*Proper assessment requires that the integrity of the sample matrix be maintained. The original sample must not be diluted more than 10% due to the spike process.

*The analytical system response from the sample the sample plus the spike should be in the same range as the sample set undergoing analysis, ideally approximating 50-75% of a full scale response.

*A matrix spike should be analyzed once for every 10 samples.

*Matrix spikes can not be performed on lab or field blanks.

*The percent recovery of analyte from the matrix spike sample is calculated using the following equation:

Matrix Spike Recovery = (SSR - SR) / SA *100

where,

SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

*If the spike recovery is outside the range in Table II 3, the spike analysis is repeated after checking

for obvious sources or error. At a minimum, this involves an immediate repeat of the instrumental analysis. If the result is still beyond acceptance limits, and tha analytical process employed a digestion step, the matrix spike should be reanalyzed including redigestion. If the recovery of the replicated sample spike continues to remain out of the designated range, the recover problem is judged to be matrix related. It is considered a non-system problem, requiring no further corrective action.

*The receovery of a matrix spike should be reported with the concentrations of the background sample and the known, theoretical spike.

3) Laboratory Replicates

*Laboratory replicate analyses provide a measure of laboratory precision. Duplicates are prepared by taking two aliquots for analysis from a well homogenized sample. More replicates may be analyzed and reported.

*A laboratory replicates should be analyzed once for every 10-20 CBP samples preferably, however every 20 samples is acceptable for those instances where the concentrations are low and this is the total sample number.

*The precision is measured by culculating the coefficient of variation (CV) using the fillowing equation:

where,

CV = Coefficient of variation
SD = Standard deviation
Mean = Mean of replicate readings
N = Number of Samples

*If the CV does not fall whithin the range in Table II.3, corrective action should be taken.

4) Check Standard

*An accurately prepare chemical standard is analyzed every 10 CBP samples preferably, however every 20 samples is acceptable for those instances where the concentrations are low and this is tha total sample number. The results are compared to the known analyte concentration. If the determined concentration for known analysis is not within 90-110% of the known analyte concentration, a second check standard is prepared and analyzed to confirm or deny the initial "out of control" analysis. If the reanalyzed check standard is within acceptance limits, sample analysis proceeds;

however, if the reanalyzed check standards fails the acceptable limits, the instrument must be recalibrated. All the samples between that checks standard and the previous standard must be reanalyzed.

5) Glassware Cleaning

*Standard and Reagent Glassware should be rinsed with 10% HCl once and then rinsed 3 times with reagent grade water.

*Sample Containers should be rinsed with tap water, 10% HCl and then rinsed 4 times with reagent water. Then, before use they should be rinsed 3 times with sample.

*Auto Analyzer Caps should be rinsed three times with the sample, and then filled.

6. Calibration and Maintenance

Maintenance and calibration of the field equipment is one of the most important issues on the monitoring activity. Without adequate management of maintenance and protection, all equipment is easily damaged.

Comments

Maintenance and calibration of the field equipment is basic and easy but one of the most important issue on the monitoring activity. Especially in KSA, where the maintenance work is more important than in other countries because of the following environmental factors. These are distinctive in KSA and can cause a rapid deterioration of the materials of the field equipment.

- Strong Sunlight (Ultraviolet rays)
- High Humidity
- High Salinity of seawater
- Dust and Sand

6.1 General matters

1) Qualified Staff

Without adequate management of maintenance and protection, all equipment is easily damaged. Thus, only qualified persons who have adequate knowledge for the equipment should manage maintenance and calibration works. Only under the supervision of the qualified person, can labor maintain and/or clean the equipment.

2) Maintenance

The frequency of maintenance depends mainly on the kinds of equipment and/o the frequency of their usage.
However, all equipment should be checked and maintained regularly, especially routine maintenance and calibration during the period of field surveys.

One of the most important issues on the field equipment maintenance is to keep all equipment clean, tidy and calibrated.

Equipment cleanness is an essential factor in ensuring that samples remain contamination - free. All sampling devices must be cleaned and/or washed with fresh water before and after each sampling trip, and stored in new plastic bags or in clean boxes.

3) Calibration

Calibration should be conducted before the survey and it its better to calibrate again after one week and/or after the survey to check the instrument worked correctly in the field. Also, calibrations should be carried out at the time of installation and/or after repairing.

In general, "Zero" solution and "Range (Span) solution are usually used for the calibration of the water quality measurement instrument.
A "Zero" solution is the standard solution used to fix the zero (or basic) point of the instrument.
A "Range" (Span) solution is used to fix the slope, range, or scale value of the instrument.
The accuracy of the concentration of these solutions is important to carry out the calibration correctly, so these solutions should be stored fresh and properly (check "use-by" date and store according to label instructions).

Calibration should be conducted under clean and tidy conditions to avoid contamination, and always use fresh standards. Do not let anyone tamper with the solutions.

All glassware and/or tools that are used for the calibration also should be kept clean.
The temperature of the Standard solution should be kept stable during the calibration. Generally, provide sufficient time for thermal stabilization on the standards. To reduce the time for stabilization, try to keep all calibration standards and instrument stored at the same temperature for at least 2 hours before the beginning of the calibration.
Standard solutions will contaminate with exposure to air so they should be kept in a container with an airtight lid when not in use.

4) Equipment Storage

Equipment should be stored in cool, shady and dry conditions after cleaning and/or washing.
If equipment is not used for a log time,
- For some metal parts such as spring, bolts, shackle etc, wipe each part with clean cloth and spray a small amount of "Moisture prevention liquid (=corrosion inhibitor such as WD40/CRC)" to prevent the rust.
- Remove the batteries from equipment.----They can leak and corrode terminals.

6.2 Maintenance and Calibration of Each Equipment

1) Van Dorn water sampler

a. Description

The Van Dorn water sampler is used to collect water samples from a depth of more than 2 meters. The sampler is composed of rubber strings and lids, stainless steel parts and high density polyethylene tube. Sampling carried out by the dropping of the "messenger" along the rope to close the Rubber lids with the power of the rubber strings.

b. Maintenance

Wash the sampler with fresh tap water before and after the survey to fully remove salt and dirt.

When sampling for trace substances, the sampler should be rinsed two or three times with distilled water after washing with tap water.

The Messenger also should be thoroughly washed and checked after the survey. After that, spray with "Moisture prevention liquid" to the moving parts of the messenger.

The sampler should be stored in the open position to prevent moisture being trapped. Possible deterioration of the rubber parts and corrosion of the steel parts (including the messenger) should be checked periodically.

2) Eckman grab sediment sampler

a. Description

The Eckman grab sediment sampler is generally used for sampling of sediments in shallow water area (<10m). The sampler has spring-tensioned, coop-like jaws on the bottom and is made from stainless steel.

The sapling is carried out by dripping of the "messenger" along the rope to close the jaws with the tension of the spring.

b. Maintenance

Wash the sampler with fresh water before and after the survey. Spray the "Moisture prevention liquid" to the moving parts of the sampler when not in use.

The "Messenger" also should b e washed and checke3d after the survey. After that, spray with "Moisture prevention liquid" to the moving parts of the messenger.

The corrosion on the steel parts (including the messenger) should be checked.

3) Van Veen grab sediment sampler

a. Description

The Van Veen grab sediment sampler is generally used for the sampling sediments from deep water areas (>10m). This sampler is also suited to the collection of hard bottom material such as sand, gravel and firm clay.

The sampler is made of stainless steel and consists of a pair of jaws and arms plus a stainless steel closing chain.

The jaws are held open by a trigger. Upon impact with the sediment, the trigger is released and the jaws are closed by the tension of the rope, which acts on the closing chain.

The arms must be strongly tightened, with the "T" key in the hole. Otherwise the lock mechanism cannot be used.

b. Maintenance

Wash the sampler with fresh water before and after the survey.

Spray with the "Moisture prevention liquid" to the moving parts of the sampler when not in use.

The corrosion of the steel parts (including the messenger) should be checked for periodically.

4) Soil sampler

a. Description

The soil sampler comprises a polycarbonate tube plus 2 silicon end caps.

The sampler is used to collect core samples and/or to collect the surface samples of exposed intertidal sediments.

b. Maintenance

Wash the tubes and caps with fresh water before and after the survey.

For sampling trace substances, the sampler should be first washed using a laboratory detergent. After that, dip into 5% HCl (Analas Grade) for one night and then rinse three times with distilled water.

For trace substances, a new sampler should be used from each site.

5) Plankton net

a. Description

The small plankton net is used for plankton sampling where only qualitative data or a large biomass is needed for analysis of plankton populations.

The plankton net comprises a tow line, nylon mesh "bolting" cloth, tap and plastic collecting cylinder.

b. Maintenance

Hang the net and wash by hosing down with lots of the tap water after the survey.

The collecting cylinder and tap should be detached from the net and washed separately.

Check regularly for corrosion of tap and other metal parts. Use a @Moisture prevention liquid " spray to prevent corrosion.

6) Water current meter

a. Description

The portable electromagnetic water current meter has no moving external parts and is used for the real-time monitoring of current speed and direction. The portable current meter comprises a Sensor Sonde, Display Unit and cable.

Power can be supplied by AC 100 or by self-contained rechargeable battery inside the display unit.

b. Maintenance

Check and recharge the Battery before and after the survey, or weekly if the survey period is long.

After the survey, the current speed sensor and connecting cable should be rinsed in fresh water first. Then carefully rinse away with cleanser and any oil or the like from the surface of the parts of the Sensor and cable.

For the Display Unit, wipe by the soft cloth with fresh water and remove the salt. Pay particular attention to the cable connectors. Make sure they are clean and spray a "Moisture prevention liquid " before storage.

When the instrument is not used for long time of period, the Battery voltage may drop. In this case, follow the battery rejuvenation procedure described in the manual.

c. Calibration

This meter is factory-calibrated so only a zero point adjustment (for confirmation)is needed.

The Zero point adjustment can be done by turning the Zero-Adjust Trimmer when the sensor is submerged in completely still water (for example- in a large sink or large bucket).

7) Portable multi-probe meter (Hydrolab DS4)

a. Description

The Hydrolab portable multi-probe meter is used to spot measure pH, temperature, DO, turbidity and Salinity at the surface and at depth.

This meter has both internal battery (9.5V) inside the meter and an external (12V) rechargeable battery pack.

b. Maintenance

General

Check and recharge the internal and external batteries before the survey.

For temporary storage, fill the sensor cup with clean tap water (don't use the distilled water) and screw the cup on the multi probe. For long term storage (>month) follow instruction manual (= Store upright with only 3cm of the water in the cup). Lay the cable coils of at least 15cm in diameter at the bottom of the container.

pH sensor

The pH glass electrode should be gently cleaned when it is obviously coated with oil, sediment or biological growth. Slow response or non-reproducible measurements are sign that the electorode has become dirty or is scratched. Carefully clean the pH glass electrode using a clean, soft cloth with methanol to remove the film from the surface of the electorode. **Never put methanol in the cup** (this will destroy the DO prove!).

DO sensor

DO sensor maintenance is usually required when calibration becomes impossible or whn the membrane covering the cell becomes wrinkled, bubbled, torn, dirty, or otherwise dameged. The membrane of the sensor should be replaced according to the procedure described in the Manual. After replacing the membrane, allow it to soak overnight in the tap water before calibration. Never use Methanol or other solvent to wash the membrane. Use a gentle spray of distilled water only.

Temperature, Salinity sensor

The temperature sensor and salinity sensor does not require any special maintenance, except to keep clean and check for possible corrosion. Do not spray with "Moisture prevention liquid"---This will badly affect the pH and DO prove.

Turbidity sensor

Turbidity sensor maintenance is required when any of the lenses have a visible coating of dirt. Rinse sensor with distilled water directed at the lenses to remove any large caked deposits and loose residue. Use soft lint cloth with methanol to remove any additional residue such as sand or grit. Be very careful not to scratch the lenses.

Wet the cloth with methanol.. Wipe the lenses and be careful not to tough DO probe. Rinse the sensor and lenses with distilled water again, then dry.

b. calibration

pH sensor

Calibration for pH is achieved by pouring a standard solution into the sensor cup. Then allow time for the solution to stabilize, and check/adjust the value of the standard according to the manual

instructions.

Generally, calibrate "Zero point" with the "zero" standard solution (pH7) first. Then calibrate the "Slope" with a "slope standard solution (pH4 and/or pH9).

The pH value of the slope standard solution used for the calibration should be better to close the value that of the anticipated samples that will be measured in the field survey. pH 9 is best for sea water monitoring programs.

DO sensor

The basic procedure of Dissolved oxygen(DO) calibration is similar to that of pH sensor. Pore the standard solution into the calibration cup. Then enter the calibration value after stabilize the value. First add sodium sulphite to sensor cup (2g) then fill to brik with distilled water and screw onto probe. Make sure there is minimum air bubble. Wait until DO reading has reached 0% saturation (10 to 15 minutes). If not stabilized, wait again. If stabilized above 0%, adjust zero according to Scout panel display (or computer link-refer manual). Then thoroughly wash cup and total probes with fresh water to remove every trace of Na2(SO3). Then use air (or shake) to get 100% saturation check.

Temperature, Salinity sensor

Temperature and salinity done not require any calibration. These sensors are factory-calibrated.

Turbidity sensor

Turbidity sensor calibration must be done in a vessel with **at least a 2 inch clearance between the vessel wall and the sensor's face**. Prepare the zero (distilled water) and slope standards. The slope standard would be close to the expected NTU value of the deployment site (20 or 50 NTU is good).

8) Portable ORP meter

a. Description

The portable ORP meter and prove is used to measure the Oxidation Reduction Potential of the sediment. This is a measure of the ability of the sediment to remove oxygen from the water. Using the lower the value (-mV)---the bigger the capacity to remove oxygen.

b. Maintenance

After the survey, the ORP prove should be rinsed in fresh water.

For the Display Unit, wipe by the soft cloth with fresh water to remove the salt and dirt. When the meter is not used for long time of period, the batteries should be removed.

c. Calibration

The portable ORP meter does not require any calibration. The probe is factory-calibrated.

9) Secchi plate

a. Description

The Secchi plate is a white and black plastic plate (30cm diameter). The plate used to measure water Clarity (by meters depth from surface).

b. Maintenance

Wash the plate with fresh water after the survey. Regularly check the connections to the tapeline and lead weight for corrosion. All shackle connections should be washed in tap water, dried and sprayed with a "Moisture prevention liquied" before storage.

10) Portable GPS

a. Description

The Portable GPS unit is used for navigating and taking position of the sampling site. The default setting is WGS84-but many spheroids are available for selection, according to the chart that is used.

b. Maintenance

Wipe by the soft cloth with fresh water and remove the salt.

When the GPS is not used the long time of period, the batteries should be removed.

The GPS unit is particularly sensitive to heat because of the microprocessor chip and the color LCD crystal display. This unit must be protected from sunshine always.

6.3 Record Keeping

When any equipment is installed, used, repaired, maintained or calibrated, details of these works should be recorded. A record sheet should be prepared for each piece of equipment and kept at MEPA by the person responsible for managing all field equipment. The manager of equipmnent should check theses records periodically and confirm that the works are being implemented properly. Examples of the recording sheet are attached.

Equipment Repair Record Sheet

Equipment Name	
Manufacturer/Model No.	
MEPA's Control No.	
Repaired Date	
Repaired Person/Company	
Responsible person (Signature)	
Symtoms and Cause	
Repaired Matters/Parts (detail extent of repairs)	
Results of Repair	
Other Remarks	

Calibration Record Sheet (pH)

		Calibration Results with Standard Solutions						Remarks
		pH7		pH4		pH9		
Date	Person	Before	After	Before	After	Before	After	

Maintainance Record Sheet

Equipment Name	
Manufacturer/Model No.	
MEPA's Control No.	
Maitainance Date	
Maintainance Person/Company	
Responsible person (Signature)	

Detail content of Maintainance

Maintained Items	Eqauipment Condition	Description
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10.		
11.		
12.		

<Legend for Equipment Condition >
G: Good CA: Calibrated/Adjusted PC: Parts Changed R: Repaired NR:Need to Repair

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Appendix

List of Analysis Procedure - Water

1	**Chlorine-Residual (Cl^-)**
2	**TOC**
3	**NH3**
4	**TKN**
5	**T-P**
6	**CN**
7	**Mg**
8	**Metals (Cd, Pb, Cu, Zn, Ni and Co)**
9	**Cr**
10	**Hg**
11	**As**
12	**Phenol**
13	**Oil & Grease**
14	**TPH**
15	**BTEX**
16	**Chlorophyll**
17	**Coliform**

Chlorine-Residual (Cl^-) ------→ **DPD colorimetric method by potable meter (SM4500-Cl G)**

Titrimetric Method

[Apparatus]

- Erlenmeyer flask (500 ml)
- Burette

[Chemicals]

① Potassium Iodide

② Acetic Acid (1+1)

③ Starch solution (10 g/L) – dissolve Starch 1 g in boiling water 100 ml

④ Sodium Thiosulfate solution (0.1 mol/L)

dissolve sodium thiosulfate 26 g and sodium carbonate 0.2 g in 1 liter of water
Stand in airtight container at least 2 days. Then standardize this.

⑤ Sodium Thiosulfate Working solution (10 m mol/L)

Take 25 ml aliquot of 0.1 mol/L solution④ into 250 ml volumetric flask and fill up with water. Prepare this solution when it's needed and use this within 12 hrs.

[Operation Flow]

Aliquot of Sample 200 – 250 ml of sample into 500 ml flask

↓

← potassium iodide ① about 1 g

← acetic acid (1+1)② about 5 ml

↓

Mix gently

↓

Stand in dark place, 5 min.

↓

Titrate ← sodium thiosulfate working solution (10 mmol/L) ⑤

When the solution turns to faint yellow, add Starch solution ③ about 1 ml as indicator.

And titrate until blue color disappears

(Blank Test)

take 100 ml of water and carry out the whole procedure

Calculate the concentration of residual chlorine in the sample as follows:

$$C = (a - b) \times f \times \frac{1000}{V} \times 0.3545$$

C: residual chlorine (mg·Cl/L)
a: 10 mmol/L sodium thiosulfate needed for titration (ml)
b: 10 mmol/L sodium thiosulfate needed for blank test (ml)
f: factor of 10 mmol/L sodium thiosulfate solution
V: volume of sample (ml)
0.3545: residual chlorine equivalent to 1 ml of 10.0 mmol/L sodium thiosulfate solution (mg)

Standardization of 0.1 mol/L sodium thiosulfate solution

Potassium Iodate
↓
Heat at about 130 °C, 2 hrs
↓
Cool in a desiccator about 30 min.
↓
Weigh about 0.72 g (record this weight)
↓
Dissolve in 200 ml volumetric flask with water
↓
Fill up to marked line with water
↓
Aliquot take 20 ml into 300 ml Erlenmeyer flask
↓ ← Potassium Iodide about 2 g
↓ ← sulfuric acid (1+5) about 5 ml
Mix and stand mix gently, stand in dark place for 5 min.
↓ ← water about 100 ml
Titrate ← sodium thiosulfate solution (0.1 mol/L)(4)

When the solution turns to faint yellow, add Starch solution ③ about 1 ml as indicator.
And titrate until blue color disappears

Separately, carry out blank test with water under the same condition.

Calculate the factor (f) of 0.1 mol/L sodium thiosulfate solution as follows:

$$f = a \times \frac{b}{100} \times \frac{20}{200} \times \frac{1}{x \times 0.003567}$$

a: amount of potassium iodate (g)

b: purity of potassium iodate (%)

x: volume of 0.1 mol/L sodium thiosulfate needed for titration (ml)

(measured value) – (blank value)

0.003567: potassium iodate equivalent to 1 ml of 0.10 mol/L sodium thiosulfate

Total Organic Carbons (TOC) – SM 5310B

Auto Analyzer

[Apparatus]

- 100 ml volumetric or Erlenmeyer flask
- TOC Analyzer (TOC-5000A)

[Chemicals]

(1) Hydrochloric Acid (1+1)

(2) Total Carbon Standard solution(50 mg/L):

take Potassium Hydrogen Phthalate exact 2.125 g and dissolve into water and make it exact 1000 ml

(3) Inorganic Carbon Standard solution (50 mg/L):

take Sodium Hydrogencarbonate exact 3.50 g and Sodium Carbonate exact 4.41 g and dissolve water and make it exact 1000 ml

(4) Water: use fresh MilliQ water

[Operation Procedure] – NPOC measurement
(Non-Purgeable Organic Carbons)

1. Sample preparation
   If dilution is required, concentration of TOC is more than 40 mg/L, dilute sample solution with volumetric pippet and 100ml volumetric flask.
   For dilution, use "fresh" MilliQ water.
   If dilution is not required, take approx. 100ml sample solution to Erlenmeyer flask.
2. Put HCl (1) 0.5 ml into flask and mix.
   pH of solution must be less than pH 3
3. insert sample uptake tube into flask or beaker, and cap with aluminum foil.
4. Measure sample solution according to the daily operation manual.

Ammonia (NH_3) – SM 4500-NH_3 B, F

Distillation-Phenate Method

[Apparatus]

- Distillation apparatus
- Tall beaker (250 ml)
- Test Tube with stopper (50 ml)
- Spectrophotometer

[Chemicals]

① Sulfuric Acid (0.04N)

sulfuric acid 1.0 ml ⟶ 1000 ml

② Borate buffer solution

NaOH(4g/L) 88ml + Sodium tetraborate($Na_2B_4O_7$ 9.5g/L) → 1000ml

③ NaOH (6 N) : NaOH 120g → 500ml

④ NaOH (1 N) : NaOH 20g → 500ml

⑤ Phenol solution: [prepare weekly]

11.1 ml of liquefied Phenol (>89%) with Ethyl alcohol → 100ml

⑥ Sodium Nitroprusside solution (0.5%): [store in amber bottle for up to 1 month]

Sodium nitroferricyanide 0.5 g → 100ml

⑦ Alkaline citrate: Tri-sodium citrate 100 g + NaOH 5 g → 500ml

⑧ Sodium hypochlorite: commercial solution about 5% [replace every 2 months]

⑨ Oxidizing solution [prepare daily]

Alkaline citrate ⑦ 20ml + Sodium hypochlorite⑧ 5ml

⑩ Ammonia Standard solution (1 N-mg/ml, 1.22 NH_3-mg/ml)

Ammonium Chloride, dried 3.819 g ⟶ 1000 ml

[Operation Flow]

Aliquot of Sample — *Blank Test*

↓ Neutralize 300 ml (V) of sample by 6N NaOH③, then pour into distilling flask

↓ ← Borate buffer② 20 ml through funnel

Distillation — in advance put sulfuric acid ① 50 ml into receiver (tall beaker)

pipe-tip of condenser should be kept below the surface

↓ heat distilling flask with several pieces of boiling chips

↓ Collect at least 150 ml distillate to receiver, neutralize with 1N NaOH④

↓ then dilute to 250 ml with water — *Standards*

Aliquot — put 25 ml of distillate into 50 ml test tube

↓ ← phenol solution ⑤ 1 ml

↓ ← sodium nitroprusside solution ⑥ 1 ml

↓ ← oxidizing solution ⑨ 2.5 ml

.NH3.doc1

Mix quietly

↓

Stand about 1 hour, in subdued light

↓

Spectrophotometer wavelength: 640 nm

(Standard Curve)

Prepare a series of standards by pipetting suitable volumes of standard solution into 50 ml test tube and dilute to 25 ml with water.

standard solution ⑤
0 µl (N-µg)
10
20
50
100

(Calculation)

$$C = \frac{a \times 250/25}{V} \times 1.22$$

C: NH_3 concentration of sample (mg/L)
a: calculated value from the standard curve (N-µg)
V: sample volume used for distillation (ml)

Total Kjeldahl Nitrogen (TKN) – SM 4500-N_{org} B

Macro-Kjeldahl Method except Ammonia removal

[Apparatus]

- Kjeldahl flask (300 ml)
- Distillation apparatus
- Tall beaker (250 ml)
- Test Tube with stopper (50 ml)
- Spectrophotometer

[Chemicals]

① Digestion reagent

Potassium Sulfate 134 g
Copper Sulfate 7.3 g → 800 ml → 1000 ml
Sulfuric Acid 134 ml

② Sodium hyroxide – sodium thiosulfate solution

NaOH 500 g + $Na_2S_2O_3 5H_2O$ 25 g → 1000 ml

③ Sulfuric Acid (0.04N)

sulfuric acid 1.0 ml ⟶ 1000 ml

④ Borate buffer solution

NaOH(4g/L) 88ml + Sodium tetraborate($Na_2B_4O_7$ 9.5g/L) → 1000ml

⑤ NaOH (6 N) : NaOH 120g → 500ml

⑥ NaOH (1 N) : NaOH 20g → 500ml

⑦ Phenol solution: [prepare weekly]

11.1 ml of liquefied Phenol (>89%) with Ethyl alcohol → 100ml

⑧ Sodium Nitroprusside solution (0.5%): [store in amber bottle for up to 1 month]

Sodium nitroferricyanide 0.5 g → 100ml

⑨ Alkaline citrate: Tri-sodium citrate 100 g + NaOH 5 g → 500ml

⑩ Sodium hypochlorite: commercial solution about 5% [replace every 2 months]

⑪ Oxidizing solution [prepare daily]

Alkaline citrate ⑦ 20ml + Sodium hypochlorite⑧ 5ml

⑫ Ammonia Standard solution (1 N-mg/ml, 1.22 NH_3-mg/ml)

Ammonium Chloride, dried 3.819 g ⟶ 1000 ml

[Operation Flow]

Blank Test

Aliquot of Sample put V ml (200ml) of sample into Kjeldahl flask or beaker

← (a couple of glass beads)

← Digestion reagent ① 50 ml

Digestion heat and boil in mantle under fume hood

↓ continue digestion until the color change to pale green about 30 minutes
after white fumes are observed

Cool in room temperature

↓

Adjust fill up to 250 ml by water

↓ ←sodium hydroxide – sodium thiosulfate solution ② 50 ml through funnel

Distillation in advance put sulfuric acid ③ 50 ml into receiver (tall beaker)
pipe-tip of condenser should be kept below the surface

↓ heat distillting flask with several pieces of boiling chips
Collect at least 150 ml distillate to receiver,
then dilute to 250 ml with water

Aliquot put 25 ml of distillate into 50 ml test tube

Standards

↓ ← phenol solution ⑦ 1 ml
← sodium nitroprusside solution ⑧ 1 ml
← oxidizing solution ⑪ 2.5 ml

Mix quietly

↓

Stand about 1 hour, in subdued light

↓

Spectrophotometer wavelength: 640 nm

(Standard Curve)

Prepare a series of standards by pipetting suitable volumes of standard solution into 50 ml test tube and dilute to 25 ml with water.

standard solution ⑤
0 µl (N-µg)
10
20
50
100

(Calculation)

$$C = \frac{a \times 250/25}{V}$$

C: TKN concentration of sample (N-mg/L)
a: calculated value from the standard curve (N-µg)
V: sample volume used for Kjeldahl digestion (ml)

Total Phosphorus (TP) -- SM 4500 (P) B & E

Spectrophotometric Method

[Apparatus]

- Digesting Bottle (100 ml)
- Autoclave
- Volumetric Flask (50 ml)
- Spectrophotometer

[Chemicals]

① Phenolphthalein indicator aqueous solution

② Potassium Persulfate

③ Sulfuric Acid (5N)

H_2SO_4 35ml → 250 ml

④ Potassium antimonyl tertrate solution

potassium antiminyl tertrate 0.686g → 250 ml

⑤ Ammonium molybdate solution

ammonium molybdate 10g → 250 ml

⑥ Ascorbic acid (0.1 M)

ascorbic acid 1.76g → 100 ml

⑦ Combined reagent - mixed in the following order - stable 4 hours

Sulfuric acid (5N) ③ 50 ml

Potassium antimonyl tertrate solution ④ 5 ml

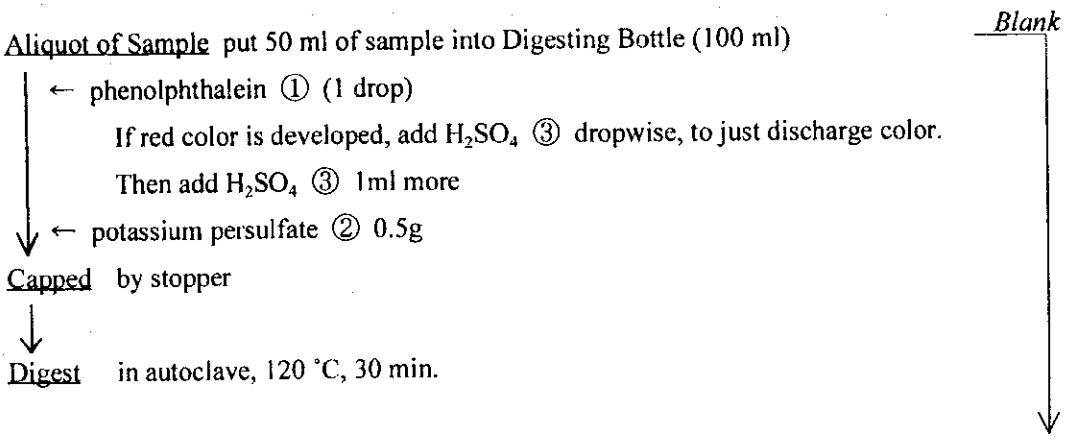
Ammonium molybdate solution ⑤ 15 ml

Ascorbic Acid ⑥ 30 ml

⑧ Phosphorus Reference Solution (50 μg-P/ml): - store in cool & dark

Potassium Dihydrogen Phosphate (dried at 105 ℃, 2 hr) 0.220g → 1000 ml

[Operation Flow]



T-P.doc 1

↓

Cool in autoclave about 2 hours

↓

Pour take 25 ml from top clear layer into volumetric flask (50ml) *Standards*

← combined reagent ⑦ 8 ml

dilute to 50 ml by water

Stand 20 – 40 °C, 15 min.

↓

Spectrophotometer using 50 mm cell, wavelength: 880 nm

(Blank Test)

take 50 ml of water and carry out the whole procedure

(Calibration Curve)

Working Solution: 2ml of standard solution ⑧ dilute to 100 ml with water

Take 2, 5 and 10 ml of working solution by pipette into 50 ml volumetric flask and proceed as the flow chart after "Pour".

Concentrations of phosphorus in these solutions are:

2.5 ml	0.05 mg/L
5.0 ml	0.10 mg/L
10.0 ml	0.20 mg/L
20.0 ml	0.40 mg/L

[Calculation]

Total Phosphorus (mg/L) = (a－b)×2

where:

a: Total Phosphorus in measured sample (mg/L)

b: Total Phosphorus in measured blank (mg/L)

2: Dilution factor (25ml→50ml)

Cyanogen (CN) – SM 4500 (CN) C&E

Spectrophotometric Method

[Apparatus]

- Distillation apparatus with aspirator
- Volumetric flask (100 ml)
- Spectrophotometer

[Chemicals]

① Sodium Hydroxide solution (1.25 N) – store in polyethylene bottle

NaOH 50 g → 1000 ml water

② Sulfamic acid

③ Magnesium Chloride solution:

$MgCl_26H_2O$ 255g → 500 ml water

④ Sulfuric acid (1+1)

Slowly add 500 ml of concentrated H_2SO_4 to 500 ml water

⑤ Sodium hydroxide dillution solution

NaOH 1.6 g → 1000 ml water

⑥ Chloramine T solution (1.0 g/100 ml water) – prepare when it is needed

⑦ Pyridine-Barbituric acid reagent:

(1) Place 15 g barbituric acid in 300 ml beaker, and add enough water to wash sides of beaker and wet barbituric acid **(Solubility of barbituric acid is not high)**
(2) Add 75 ml pyridine and mix
(3) Add 15 ml conc. HCl, and cool to room temperature
(4) Carefully pour into 250 ml volumetric flask by washing side of beaker with water (mixture is emulsion with pale yellow color, not solution)
(5) Fill up to 250ml and mixed until dissolved
(6) Store in amber glass bottle and store in refrigerator

⑧ Acetate Buffer

(1) Sodium Acetate trihydrate 82 g → 100 ml water
(2) Add gracial acetic acid to adjust pH 4.5

⑨ Cyanogen Reference solution(1 mg/ml):

NaOH 0.4 g + Sodium Cyanide 0.4711 g water → 250 ml

<< Potassium Cyanide is highly toxic >>

[Operation Flow]

Aliquot of Sample — put 500 ml of sample into distillation flask (1000 ml) — *Blank Test*

↓ ← sulfamic acid ② 2 g then mix for 3 min.

Set distillation apparatus — in advance, put 1.25 N NaOH ① 50 ml in receiver

↓

Adjust vacuum source by Aspirator, two bobbles per second from inlet tube

↓ ← sulfuric acid (1+1) ④ 50 ml through inlet tube

↓ ← magnesium chloride solution③ 20 ml through inlet tube

Distillation heat distilling flask for 1 hour and 15 min.

↓ after turn-off heating

Pour solution from receiver to 100 ml volumetric flask and fill up with water

↓ take 20 ml of solution into volumetric flask (50 ml) *Standards*

↓ ← dilute 40 ml with NaOH diluted solution

↓ ← 1 ml acetate buffer solution ⑧

↓ ← chloramine T ⑥ 2 ml

Mix & stand 2 min.

↓ ← pyridine-barbituric acid ⑦ 5 ml

Fill up fill up to 50 ml with water

↓

Stand exactly 8 min.

↓

Spectrophotometer using 10 mm cell, wavelength: 578 nm

(Standard Curve)

Working Solution: 2 ml of standard solution⑨ dilute to 200 ml with water

Take 0.5, 1, 2 and 3 ml of working solution by pipette into 50 ml volumetric flask and carry out the above procedure.

Concentrations of cyanogen in these solutions are:

0.5 ml	0.1 mg/L
1 ml	0.2 mg/L
2 ml	0.4 mg/L
3 ml	0.6 mg/L

[Calculation]

Total Cyanogen (mg/L) = (a − b) / 2

where:

a: CN found in measured sample (mg/L)

b: CN found in measured blank (mg/L)

Magnesium (Mg) – (SM 3111 B)

Atomic Absorption Spectrometric Method

[Apparatus]

- Volumetric Flask (100 ml)
- Atomic Absorption Spectrometer

[Chemicals]

(1) Hydrochloric Acid (1+1)

(2) Reference solution for Magnesium (1mg/ml)

[Operation Flow]

Aliquot of Sample — put 1 ml of sample into 100 ml volumetric flask
↓ ← hydrochloric acid (1) 2 ml
Fill up ← water, up to marked line
↓
Aliquot 1 ml into 100ml volumetric flask
↓ ← hydrochloric acid (1) 2 ml
Fill up ← water, up to marked line
↓
AAS Wavelength: 285.2 nm

(calibration Curve)

Working solution: take 1ml of Reference solution (2) into 100ml volumetric flask, and fill up to the marked line.

Take 0, 1 and 2 ml working solution into 100ml volumetric flasks respectively and add 2ml of hydrochloric acid, then fill up to the marked line. These concentratoins are 0, 0.1 and 0.2 ppm.

[Calculation]

$$Mg\ (mg/L) = a \times (100 / 1) \times (100 / 1)$$

where;

a: Mg found in measured solution (mg/L)

(100 / 1): dilution factor

Metals (Cd, Pb, Cu, Zn, Ni and Co) – (SM 3111 C)

Extraction-Flame AAS

[Apparatus]

- Conical beaker (500 ml)
- Separating Funnel (250 ml)
- Hot Plate
- Shaker
- Atomic Absorption Spectrometer

[Chemicals]

(1) Hydrochloric Acid

(2) Ammonium Hydroxide (1+1)

(3) m-cresol purple solution (1 g/L)

(4) Ammonium Sulfate solution (saturated)

(5) Ammonium Pyrrolidine dithiocarbamate (APDC: 10 g/L)

(6) 2,6-Dimethyl-4-Heptanone

(7) Reference solution for each metal

[Operation Flow]

Aliquot of Sample — 250 ml of sample into 500ml conical beaker

↓ ← hydrochloric acid (1) about 5 ml

Heat — hot plate, boiling for about 5 min.

↓

Cool — room temperature

↓ ← few drops m-cresol purple solution(3)

Adjust pH — pH 3.0 <-- ammonium hydrate (2) and hydrochloric acid (1)
at the end point, color of solution is bright yellow

↓

Transfer into separating funnel 250ml

↓ ← ammonium sulfate (4) about 10 ml
← APDC (5) about 5 ml

Mix — gently

↓

Stand — 3 min.

↓ ← 2,6-dimethyl-4-heptanone (6) exact 25 ml

Shake — about 3 min.

↓ → water phase (discard)

Organic phase into test tube with glass stopper

↓

Measurement

AAS	Element	Wavelength
	Cd	228.8 nm
	Pb	283.3 nm
	Cu	324.8 nm
	Zn	213.8 nm
	Co	240.7 nm
	Ni	232.0 nm

(Standard Curve)

Take about 200ml water into three separating funnels (250ml) respectively and add next amount of standard solution. Proceed flow chart after "adjust pH".

(μg)

Element	Standard 0	Standard 1	Standard 2
Cd	0	10	20
Pb	0	100	200
Zn	0	10	20
Cu	0	40	80
Co	0	50	100
Ni	0	50	100

Concentrations of standard solution (after extraction) are

(mg/L)

Element	Standard 0	Standard 1	Standard 2
Cd	0	0.4	0.8
Pb	0	4	8
Zn	0	0.4	0.8
Cu	0	1.6	3.2
Co	0	2	4
Ni	0	2	4

[Calculation]

Metal (mg/L) = (a – b) × 25 / v

Where;

a: metal found in measured sample organic solvent (mg/L)

b: metal found in measured blank organic solvent (mg/L)

25: volume of organic solvent (ml)

v: sample volume taken (ml)

Chromium (Cr)

Extraction-Flame AAS

[Apparatus]

- Conical beaker (250 ml)
- Separating Funnel (250 ml)
- Hot Plate
- Shaker
- Atomic Absorption Spectrometer

[Chemicals]

(1) Sulfuric Acid (1+1)

(2) Potassium Permanganate (50 g/L)

(3) Hydroxylamine hydrochloride solution (100 g/L)

(4) Tri-n-octylamin solution:

dissolve Tri-n-octylamin 15 g into MIBK 500 ml

(5) Cr reference solution

[Operation Flow]

Aliquot of Sample — put 100 ml of sample into 250 ml beaker

↓ ← about 5ml HNO3

Heat — boiling, for 5min.

↓ ← sulfuric acid (1+2) (1) about 2 ml

↓ ← about 10ml potassium permanganate (2)

Heat — boiling for 10 min., add potassium permanganate solution (2) to keep faint red color

↓ ← 1 or 2 drops of hydroxylamine hydrochloride solution (3)

↓ until faint red color will disappear (MnO_2 residue will remain)

Cool

↓

Pour — into 250ml separating funnel

↓ ← tri-n-octylamin solution (4) exact 20 ml

Shake — 10 min.

↓ ↓

Solvent phase — into test tube; water phase — (discard)

↓

Cr 1/2

Filtrate use dry filter paper

↓ do not rinse filter paper after filtering

AAS Wavelength: 357.9 nm

Fuel rich flame should be used

(Standard Curve)

take next amount of Cr into 200ml beaker and add about 100ml water, then proceed flow chart (add 1ml permanganate solution instead of 10 ml).

standard 0:	0(μg)	(0ppm after extraction)
standard 1:	100(μg)	(5ppm after extraction)
standard 2:	200(μg)	(10ppm after extraction)

[calculation]

$Cr = (a - b) \times 20 / v$

where;

a: Cr found in measured sample organic solvent (mg/L)

b: Cr found in measured blank organic solvent (mg/L)

20: volume of organic solvent (ml)

v: sample volume taken (ml)

Mercury (Hg) – (SM 3112 B)

Cold vapor-AAS method

[Apparatus]

- Kjeldahl Flask (300 ml)
- Volumetric Flask (200 ml)
- Water Bath
- AAS with Vapor Generation unit for Hg

[Chemicals]

(1) Sulfuric Acid (1+1)

(2) Nitric Acid

(3) Potassium Permanganate solution (5 w/v %)
dissolve potassium permanganate 50g in 1000 ml water, store in brown bottle

(4) Potassium Peroxodisulfate solution (5 w/v %)
dissolve potassium peroxodisulfate 5g in 100 ml hot water

(5) Hydroxylamine Hydrochloride solution (20 w/v %)
dissolve hydroxylamine hydrochloride 20 g into 100 ml water

(6) Hydrochloric acid (1+1)

(7) Sodium Borohydrate (0.4 w/v %)
Dissolve 0.4g NaOH into about 50ml water, and dissolve sodium borohydrate 0.4g into NaOH solution, then dilute to about 100ml with water. Keep in refrigerator.

(8) standard solution for Hg

[Operation Flow]

Aliquot of Sample put 100 ml of sample into Kjeldahl flask (300 ml)
↓ ← sulfuric acid (1+1) (1) 20 ml
← nitric acid (2) 5 ml
← potassium permanganate solution (3) 15 ml
Mix stand about 15 min., if red color disappears add (3) little by little
↓ ← potassium peroxodisulfate solution (4) 10 ml
Heat in water bath, more than 95 °C, 2 hours
↓
Cool
↓ ← hydroxylamine hydrochloride solution (5)
until color of permanganate disappears
Transfer into volumetric flask (200 ml)
↓

Fill up to 200 ml with water

↓

Aliquot into Erlenmeyer flask (100 ml)

↓

AAS with vapor generation unit

Wavelength: 253.7 nm

(Standard Curve)

prepare calibration solutions every measurement day

prepare 10 mg/L solution from stock solution (add 5ml HNO3 for 100ml solution)

make following concentration of Hg standard solution from 10 mg/L solution and measure with AAS (add 5ml HNO3 for 100ml solution)

0 µg/L
20 µg/L
40 µg/L

[calculation]

$$Hg\ (\mu g/L) = (a - b) \times 200 / v$$

where;

a: Hg found in measured solution (µg/L)

b: Hg found in measured blank solution (µg/L)

200: volume of measured solution (ml)

v: sample volume taken (ml)

Arsenic (As) – (SM 3114)

Hydride generation-AAS Method

[Apparatus]

- Beaker (100 ml)
- Volumetric Flask (50 ml)
- Hot Plate
- AAS with Hydride Generation unit for As

[Chemicals]

① Sulfuric Acid (1+1)

② Nitric Acid

③ Hydrochloric Acid (1+1)

④ Potassium Iodide solution (100 g/L) [prepare 30 minutes before use]

⑤ Sodium Borohydrate (SBH) solution:

SBH 10 g → Sodium hydroxide (4 g/L) 1000 ml

⑥ Reference solution for As

[Operation Flow]

Aliquot of Sample — put 20 - 50 ml of sample into beaker (100 ml)

↓ ← sulfuric acid (1+1)① 1 ml

↓ ← nitric acid ② 2ml

Heat — on hot plate with watch glass, 300 °C

↓ until generating white fume of sulfuric acid

Cool — in room temperature

↓ ← hydrochloric acid (1+1)③ 8 ml

Heat — on hot plate 100 °C, 1 hour

↓

Cool — in room temperature

↓

Pour — into volumetric flask (50 ml)

↓ ← potassium iodide solution ④ 8 ml, add 30 min. before analysis

Fill up — to 50 ml with water

↓ SBH solution⑤ →

↓ HCl (1+1)③ →

AAS — sample → hydride generation unit → flow cell

(Blank Test)

take 50 ml of water and carry out the whole procedure

(Standard Curve)

Make standard solution as 50 µg-As/L

→ 2, 5, 10, 20, 30 ml into volumetric flask (50 ml)

↓ ← hydrochloric acid (1+1)③ 8 ml

↓ ← potassium iodide solution ④ 8 ml

Fill up to 50 ml with water

↓

AAS with hydride generation unit

Phenols – US.EPA 420.1

Spectrophotometric Method

[Apparatus]

- Distillation apparatus
- Separating funnel (500 ml)
- Test tube with stopper (50 ml)
- Spectrophotometer

[Chemicals]

① Methyl Orange (0.05 g/50ml)

② Phosphoric Acid (1+9)

Dilute 10 ml of 85% H_3PO_4 to 100ml water

③ Copper Sulfate solution (100 g/L)

Dissolve 25 g $CuSO_4 \cdot 5H_2O$ in 250 ml water

④ Buffer solution (pH 10):

Dissolve 16.9g of Ammonia chloride in 143 ml Ammonium hydroxide and dilute to 250ml with water

⑤ Potassium ferricyanide {hexacyanoferrate(III)} solution (80 g/L): store in refrigerator

Dissolve 8 g $K_3Fe(CN)_6$ in 100 ml water

⑥ 4-Aminoantipyrine solution (20 g/L): prepare daily

Dissolve 2 g 4AAP in 100 ml water

⑦ Phenol reference solution (1.0 g/L): store in refrigerator

Dissolve 1.0 g phenol in 1000 ml water

⑧ Chloroform

[Operation Flow]

Aliquot of Sample — put 500 ml into distillation flask (1000 ml)

↓ ← methyl orange ① a couple of drops

Adjust of pH — drop phosphoric acid (1+9)② until color changes to red(pH 4)

↓ ← copper sulfate solution ③ about 5 ml

Distillation — heat distilling flask, use boiling stone

↓ until distillate will become about 450ml

Transfer — put distillate into separating funnel (500 ml) *Standards*

↓ ← ammonia chloride – ammonia buffer solution ④ about 10 ml

↓ ← potassium hexacyanoferrate solution ⑤ 3.0 ml

↓ ← 4-aminoantipyrine solution ⑥ 3.0 ml

Mix
↓
Stand 3 min.
↓ ← chloroform ⑧ 10 ml
Extract shake 1 min. (10 times ×2), then vent chloroform fumes into hood
↓ → water phase (discard)
Organic phase
↓
Filtrate use dry filter paper in fume hood
take into test tube
↓
Measure Spectrophotometer, 460 nm

(Blank Test)

take 450 ml of water and carry out the whole procedure

(Calibration Curve)

Working Solution: dilute 5 ml of reference solution⑦ to 500 ml with water

Take 5, 10 and 20ml working solution into 500ml separating funnels respectively and add about 200ml water. Proceed as the flow chart after "Transfer".

Concentrations of phenol in measured solvent are

5 ml	0.05 mg/ 10 ml of Solvent	5 mg/L
10 ml	0.10 mg/ 10 ml of Solvent	10 mg/L
20 ml	0.20 mg/ 10 ml of Solvent	20 mg/L

[calculation]

Phenol (mg/L) = (a –b)× 10/ 500

where;

a: Phenol found in measured sample (mg/L)

b: Phenol found in measured blank (mg/L)

10: volume of measured solvent (ml)

500: volume of sample taken (ml)

Oil & Grease – US.EPA 413.2

Solvent extraction – Analyzer (infrared spectrophotometer)

[Apparatus]

- Separating Funnel (1000 ml)
- Oil Contents Meter (Horiba OCMA300)
- Filter Paper, Whatman No.40

[Chemicals]

① Exclusive Solvent for OCMA300 (S-316)

② Hydrochloric Acid (1+1)

③ Oil Standard Solution (50 mg/L)

B-heavy Oil (accessory of OCMA300) 28 µl → 250 ml with solvent①

④ Sodium sulfate Na_2SO_4

[Operation Flow]

Sample — Pour sample solution (1 liter) into separating funnel (cap should be glass).
About 25 ml of solvent CFC-316① is added to sample bottle (cap should be glass)
Shake vigorously, 2 min, and pour solvent into separation funnel.
Rinsing sample bottle with about 5 ml of solvent.

↓

Shake — vigorously, 2 min.

↓

Separate

↓

solvent

↓

filtrate* use solvent-moistened filter paper
100ml flask
with glass stopper

water phase

← add about 30 ml solvent

shake 2 min.

separate

solvent — filtrate*

water phase

← add about 30 ml solvent

shake 2 min.

solvent — filtrate*

water phase (discard)

* an emulsion that fails to dissipate can be broken by poring about 1 g $Na_2SO_4$④ into filter paper cone and slowly draining the emulsion through the salt

↓

combine in 100 ml flask

↓

fill up with solvent to 100 ml

↓

Oil Contents Meter

[OCMA Operation]

1) Turn on power switch (rear side) and wait until "WARM UP" lamp goes out.

2) Press [MODE] until "AUTO MEAS" lamp lights.

3) Insert 10 ml of prepared solvent into the inlet.

4) Add one drop of hydrochloric acid② into the inlet.

5) Insert 20 ml of distillated water into the inlet.

repeat

6) Press [START] to begin the extraction.

(Calibration)

Be sure to calibrate when using a different lot of extraction solvent.

(1) Zero calibration

a. Press [MODE] until "CAL" lamp lights, then press [ENT]
b. Insert 10 ml of solvent① into the inlet
c. Add one drop of hydrochloric acid② into the inlet
d. Insert 20 ml of water into the inlet
e. Press [START] to begin the extraction

repeat

(2) Span calibration

a. After zero calibration is completed, press [▲] or [▼]to display shows "SPAN CALIB", then press [ENT]
b. Insert 10 ml of standard solution③ into the inlet
c. Add one drop of hydrochloric acid② into the inlet
d. Insert 20 ml of water into the inlet
e. Press [START] to begin the extraction

repeat

[calculation]

Oil & Grease (ppm) = (a – b) × 2 × 100 / 1000

Where;

a: concentration shown on Oil Content Meter (mg/L)

b: concentration of blank (mg/L)

2: factor to obtain concentration in solvent

100: solvent volume (ml)

1000: taken sample amount (ml)

TPH (Total Petroleum Hydrocarbons) – US.EPA 418.1

Solvent Extraction - Analyzer (infared spectrophotometer)

[Apparatus]

- Separating Funnel (1000 ml)
- Filter Paper, Whatman No.40
- Oil Contents Meter (Horiba OCMA300)

[Chemicals]

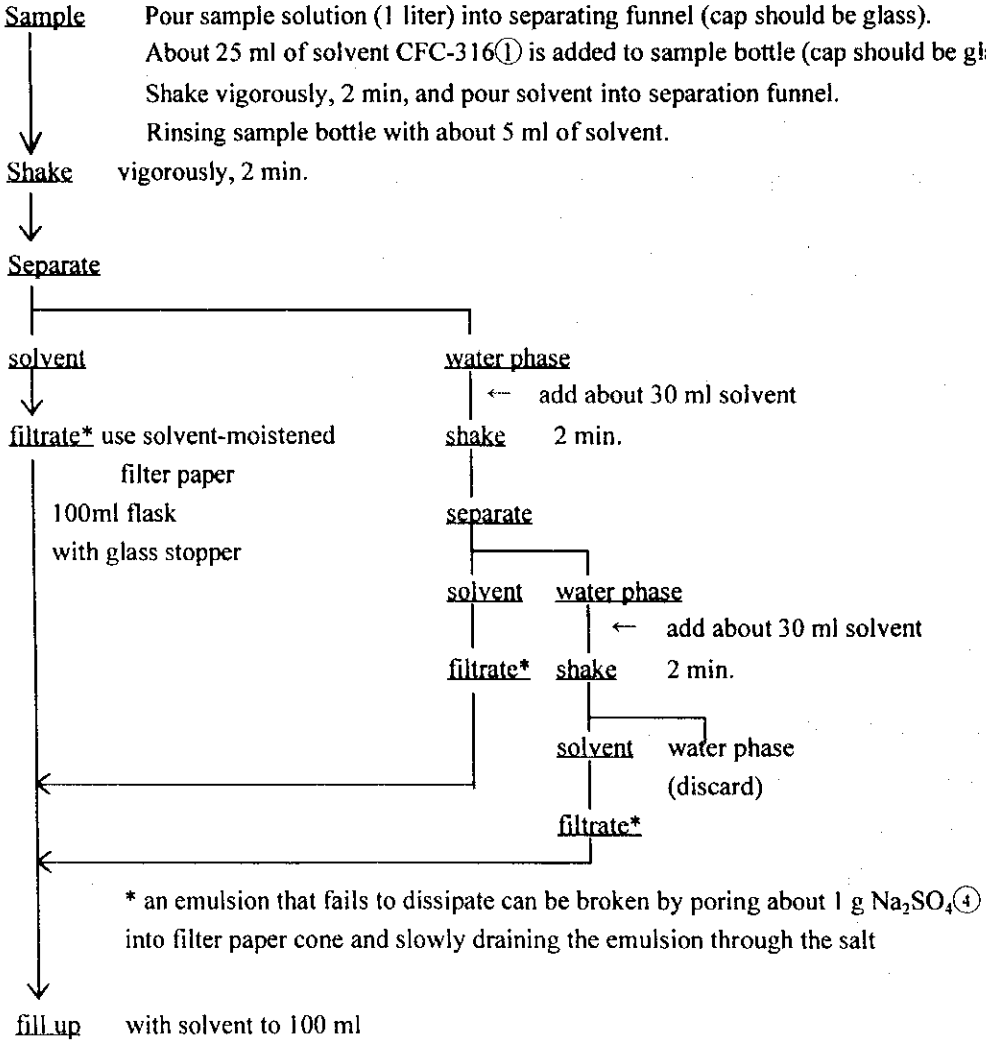
① Exclusive Solvent for OCMA300 (CFC-316)

② Silica gel (60 – 200 mesh)

③ HCl (1+1)

④ Sodium sulfate Na_2SO_4

[Operation Flow]



↓ ← **silica-gel ② 3 g**

Mix with magnetic stirrer, 5 min.

↓

filtrate

↓

Oil Contents Meter measure same as Oil & Grease procedure

[calculation]

Oil & Grease (ppm) = (a – b) × 2 × 100 / 1000

Where;

a: concentration shown on Oil Content Meter (mg/L)

b: concentration of blank (mg/L)

2: factor to obtain concentration in solvent

100: solvent volume (ml)

1000: taken sample amount (ml)

BTEX (Benzene, Toluene, Ethylbenzene and Xylene)

Gas-chromatographic Method with head space sampler

[Apparatus]

- Vial bottle (20 ml)
- Aluminum cap with PTFE septum
- Micro syringe
- GC-FID with Headspace auto-sampler

[Chemicals]

① Sodium Chloride (ground is better)

② Methanol

③ Mixed reference solution of BTEX (2 mg/ml for each)

④ Fluorobenzene (1 mg/ml): store in refrigerator

[Operation Flow]

Blank Test
Standards

Aliquot of Sample — put 10 ml of sample to vial bottle contains 3 g of sodium chloride ①

Add fluorobenzene (1 mg/L) ④ 1 µl by micro syringe,

then stopper by aluminum cap with PTFE septum

↓

GC/FID — set in headspace auto-sampler

(Blank Sample)

10 ml of water

(Standard Curve)

Working Solution: dilute 1 ml of reference solution to 10 ml with methanol (200 mg/L)

→ store in refrigerator

in advance, add 3 g of sodium chloride and 10 ml of water to vial bottle

1) add fluorobenzene (1 mg/ml) ④ 1 µl by micro syringe

2) add 1, 2 and 5 µl of working solution by micro syringe

add volume (µl)	concentration(mg/L)
1	0.02
2	0.04
5	0.10

[GC Operations]

1. Air Compressor ON
2. after air pressure comes up (> 50 kPa), turn on GC-17A
3. CBM-101 ON, Computer ON
4. GC System ON
   1) [Main Menu] open
   2) [Real time analysis]
   3) [Method file] - load: BTEX.MET
   4) Helium gas open
   5) Click System ON
   6) Wait until setting temperature comes up (see GC monitor)
5. FID Ignition ON
   1) Hydrogen gas open
   2) Click Flame ignition
   3) Wait until the baseline settled
6. Sample Analysis
   1) [Sample Schedule]
   2) [File] - Create or Load (Save as)
   3) input "Sample name", "Sample ID", "Data file", "Method file (BTEX.MET)"
   4) Click Run

{Shut Down}

1) [Method file] - load: Shut.MET
2) Hydrogen gas shut
3) Wait until the temperature comes down (column temp. < 50°C)
4) Click System OFF
5) Helium and Air shut
6) Turn off Computer, CBM off, GC off

Chlorophyll a – SM 10200 H

Spectrophotometric Method

[Apparatus]

- Glass-fiber filter paper, 47 mm diam
- Filtrate system
- Centrifuge Tube with stopper (10 ml)
- Centrifuge
- Spectrophotometer

[Chemicals]

① Magnesium Carbonate solution

Dissolve 1.0 g $MgCO_3$ to 100 ml water

② Acetone solution (90 %) – prepare when it is needed

mix 90 ml acetone with 10 ml water

[Operation Flow]

Aliquot of Sample put V liter of sample (about 1 L) into filtration funnel

↓ with magnesium carbonate solution ① 1 ml

Filtrate keep suction a few minutes after filter dried

sample on filter may be placed in airtight plastic bag and stored frozen for 3 weeks

Filter into centrifuge tube

↓ ← acetone solution ② 10 ml

Stand in cool and dark place, 1 hour

↓

Centrifuge 3000 rpm, 10 min.

↓

Pour upper layer into test tube

↓

Spectrophotometer with 10 mm cell at wavelength: 750, 664, 647 and 630 nm

Use contrast solution as Acetone solution②, measure each blank optical dencity

[Calculation]

Chlorophyll a (μg/L) = {11.85*(OD664) – 1.54*(OD647) – 0.08*(OD630)} × 10/V

OD664, 647, 630: corrected optical densities (subtracted OD750)

V: volume of sample (L)

Total Coliform – SM 9222 B

Membrane Filtration Method

[Apparatus]

- Membrane Filter (Millipore Milliflex filter funnel unit)
- Vacuum Pump (Millipore Milliflex vacuum filtration system)
- Petri Dish (Millipore Milliflex sterile culture media cassette)

[Chemicals]

1. MF-Endo Media (Millipore MF-Endo media)
2. MilliQ water: use fresh MilliQ water

[Operation Flow]

sample preparation

Aliquot of Sample — put certain volume of sample in 100ml measuring cylinder

↓

Dilution — add MilliQ water up to 100ml into cylinder

↓

Filtrate — according to the operation manual

↓

Cultivate — in incubator, 35 °C, 48 hrs

↓

Count — count red or pink colony with shine surface

See the operation manual for the detail preparation.

[Blank test]

Blank test should be implemented simultaneously with sample analysis. Use fresh MilliQ water 100ml for sample.

If colonies will be found in blank test, there is the possibility of contamination. Retest is recommended.

[Calculation]

Density of coliform = number of colonies counted × 100 / V

(number / 100ml)

Where,
V: sample volume (ml)
100 / V : dilution factor

List of Analysis Procedure - Sediment

1	**Loss of Ignition**
2	**TOC**
3	**Metals (Cr, Cd, Pb, Cu, Zn, Co, Ni and V)**
4	**Hg**
5	**As**
6	**TPH**
7	**BTEX**

Loss of Ignition – SM 2540 E

[Apparatus]

- Furnace Mantle
- Evaporating dish
- Crucible, porcelain

[Operation Flow]

A) Make dry sample

Sediment sample

↓ into evaporating dish

Dry 105 °C, 2 hours

↓

Cool in desiccator, 40 min.

↓ moisture contents = (initial weight – dried weight)/initial weight

Crush → Dry Sample

B) Ignition

Dry Sample

↓

Crucible in advance ignite at 550 °C for 1 hr and weigh the mass

↓

Weigh as sample weight 3 – 5 g

↓

Ignite in furnace, 550 °C, 2 hrs

↓

Cool after cool down in furnace, remove into desiccator for 1 hr

↓

Weigh

[calculation]

$$I = \frac{a-b}{b-c} \times 100$$

Where, I: ignition loss (%)
a: mass of dry sample with the crucible (g)
b: mass of ignited sample with the crucible (g)
c: mass of the crucible (g)

TOC in sediment – MOOPAM IV.4

[Apparatus]

- Burette, 25 ml
- Erlenmeyer flask, 500 ml

[Chemicals]

(1) H_2SO_4 with Ag_2SO_4

Dissolve 2.5g Ag_2SO_4 in 1 liter H_2SO_4

(2) $K_2Cr_2O_7$ solution (1N):

Dissolve exact 49.04g $K_2Cr_2O_7$ in water and dilute to exact 1 liter with water

(3) ferrous ammonium sulfate solution (0.5N)

dissolve 196.1g $Fe(NH_4)_2SO_46H_2O$ in 800ml water, add 20ml H_2SO_4 and dilute to 1L with water

(4) indicator (diphenylamine)

dissolve 0.5g diphenylamine in 20ml water and add 100ml H_2SO_4 to it

(5) H_3PO_4 (85%)

(6) NaF (solid)

[Operation Flow]

Dry Sediment about 0.5 g into 500 ml flask

↓

← $K_2Cr_2O_7$ solution(2), exact 10 ml

← H_2SO_4 with Ag_2SO_4 (1), 20 ml

Mix gently, 1 minute

↓

Leave 30 minutes

↓

← Water, 200 ml

← H_3PO_4, 10 ml

← NaF, 0.2 g

← indicator (4) 15 drops

↓

Titration by ferrous ammonium sulfate solution (3)

(end point: from dark violet to green)

[Calculation]

$$TOC\ (\%) = (1 - T/S) \times f \times 10$$

Where, T: sample titration (ml)

S: blank titration (ml)

f: factor

$$f = 12/4000 \times 1.72 \times 100/w$$

w: sample weight (g)

Analysis Procedure for Cr, Cd, Pb, Cu, Zn, Co, Ni and V in Sediment

[Apparatus]

- Beaker, 250 ml
- Hot Plate
- Filter Paper, 110 mm, No.1
- Funnel
- Volumetric Flask, 100 ml
- Atomic Absorption Spectrometer

[Chemicals]

(1) Nitric Acid

(2) Hydrochloric Acid

(3) Hydrochloric Acid (1+10)

[Operation Flow]

dry sample about 2 g into 200ml beaker

↓ ← HNO_3 (1) approx.10ml, little by little

↓ ← HCl (2) approx.20ml

stand until reaction will finish

↓

heat hot plate, about 150 °C,

↓ cover with watch glass, for about 30min. (never make dryness)

do not overheat, or bumping will happen

cool for 5 min.

↓ ← HNO_3 (1) approx.20ml

heat hot plate, about 150 °C,

↓ cover with watch glass, but make some space for escaping of vapor

for 30min. (never make content dryness)

do not overheat, or bumping will happen

↓

cool for 5 min.

↓ ← water approx. 30ml

heat hot plate, about 120 °C

↓ cover with watch glass, for 15 min.

↓

cool to room temperature

↓

filtrate — wash residue with HCl(1+10) (3)

residue (discard)

solution — into 250ml beaker

if color of solution is black or dark brown, stop process and ask supervisor for extra treatment

↓

heat — hot plate, about 120 °C

until volume will decrease less than 100ml

without watch glass, never make content dryness

↓

cool — to room temperature

↓

transfer — into 100ml volumetric flask

↓

fill up ← water, to marked line

↓

measure — AAS

{AAS conditions}

N_2O – C_2H_2 flame: V

Air – C_2H_2 flame: others

For Cr measurement, fuel rich flame should be used.

[Standard solutions]

HCl 2ml / 100ml solution

(mg/L)

Elements	Cal. 0	Cal. 1	Cal. 2
Cd	0	1	2
Ni	0	5	10
Cr	0	10	20
Co	0	5	10
V	0	50	100
Zn	0	0.5	1
Pb	0	10	20
Cu	0	5	10

[Calculation]

Metals (mg/L) = (a – b) × 100 / w

where;
a: metals found in measured solution (mg/L)
b: metals found in blank solution (mg/L)
100: volume of measured soution (ml)
w: amount of sample (g)

Analysis Procedure for Mercury (Hg) in Sediment

[Apparatus]

- Kjeldahl Flask (300 ml)
- Volumetric Flask (200 ml)
- Water Bath
- Glass fiber filter Paper

[Chemicals]

(1) Nitric Acid
(2) Sulfuric Acid (1+1)
(3) Potassium Permanganate solution (3 w/v %)
(4) Potassium Peroxodisulfate solution (5 w/v %)
(5) Urea solution (10 w/v %)
(6) Hydroxylamine Hydrochloride solution (20 w/v %)
(7) Hg Standard Solution

[Operation Flow]

Wet Sediment
↓
Weigh about 10 g, into Kjeldahl flask (300 ml)
← water about 40 ml
↓
Cool with water and ice bath
← nitric acid (1) about 20 ml, little by little
← sulfuric acid (1+1) (2) about 20 ml
↓
Stand room temperature, until reaction will finish
← potassium permanganate (3 w/v %) (3) about 20 ml
↓
Mix wait about 15 min.,
if red color disappears, add potassium permanganate (3) little by little
← potassium peroxodisulfate (5 w/v %) (4) about 10 ml
↓
Heat in water bath, more than 95 °C, 2 hours
↓
Cool down to about 40 °C
← urea (10 w/v %) (5) about 10 ml
← hydroxylamine hydrochloride (20w/v%) (6)
until color of permanganate disappears
↓

Filtrate glass fiber filter paper

↓

Solution into 200 ml volumetric flask

↓

Fill up with water into marked line

↓

Measurement

AAS with Vapor Generation System

Wavelength: 257.3 nm

(Standard Curve)

prepare calibration solutions every measurement day

prepare 10 mg/L solution from stock solution (add 5ml HNO3 per 100ml solution)

make following concentration of Hg standard from 10mg/L solution and measure with AAS (add 5ml HNO3 per 100ml solution)

0 μg/L
20 μg/L
40 μg/L

[calculation]

$Hg\ (mg/L) = (a - b) \times 0.2 / w$

where;

a: Hg found in measured solution (μg/L)

b: Hg found in blank solution (μg/L)

0.2: volume of measured solution (L)

w: amount of sample (g)

Analysis Procedure for As in Sediment

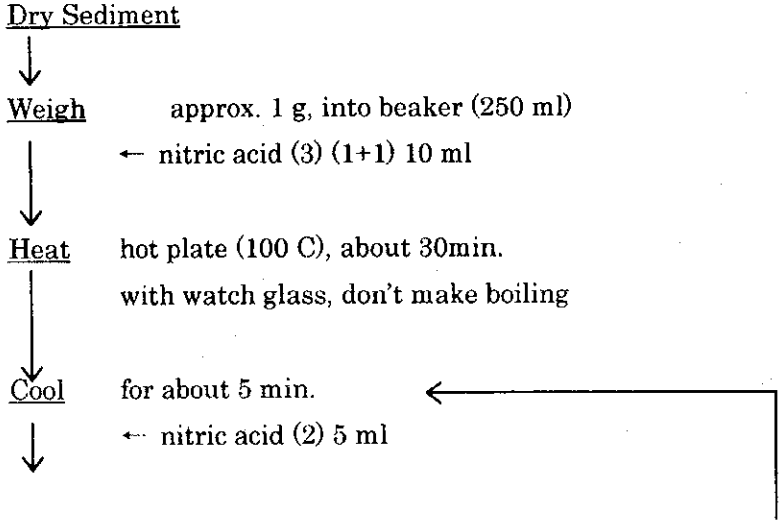
[Apparatus]

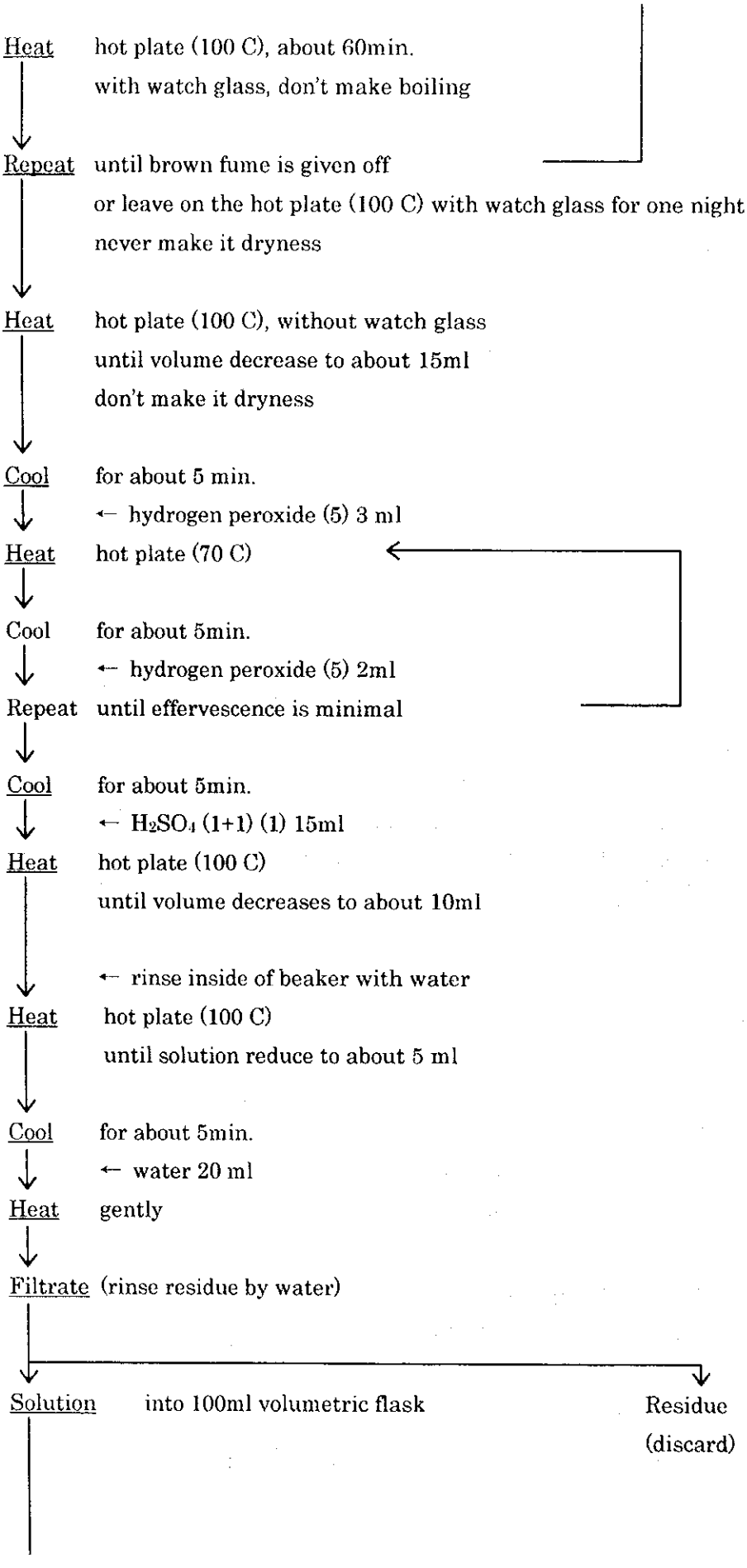
- Beaker (250 ml)
- Watch glass
- Volumetric Flask (100 ml)
- Hot Plate
- Funnel
- AAS with hydride generation system

[Chemicals]

(1) Sulfuric Acid (1+1)
(2) Nitric Acid
(3) Nitric acid (1+1)
(4) Potassium Iodide Solution (20 w/v %)
(5) Hydrogen peroxide (30%)
(6) HCl
(7) urea
(6) As Standard Solution
(7) HCl (1+2) for hydride measurement
(8) Sodium Borohydrate (SBH) solution (0.6 w/v %) for hydride measurement
Dissolve approx. 0.5g NaOH into about 100ml water, and dissolve approx. 0.6g SBH into the NaOH solution.
Keep in refrigerator.

[Operation Flow]





As in Sediment 2/2

↓ ← HCl (6) 30ml
← urea (7) 2g

← potassium iodide solution (4) (20 w/v %) 5 ml
add 30min. prior to measurement

Fill up to 100 ml with water

↓

AAS

Wavelength: 197.2 nm

[Calibration]

Take 3 volumetric flasks (100ml) and add urea 2g and HCl 30ml respectively. And add 0, 5 and 10 μg As standard solution for each flask, then add KI solution (20%) 5ml and fill up to marked line with water.
Concentration of these solution are 0, 0.05 and 0.1 mg/L respectively.

[Calculation]

Concentration of As (mg/L) = (a – b) * 100 / w

Where;
a: As concentration detected in sample solution (mg/L)
b: As concentation detected in blank solution (mg/L)
w: sample weight (g)

TPH in sediment

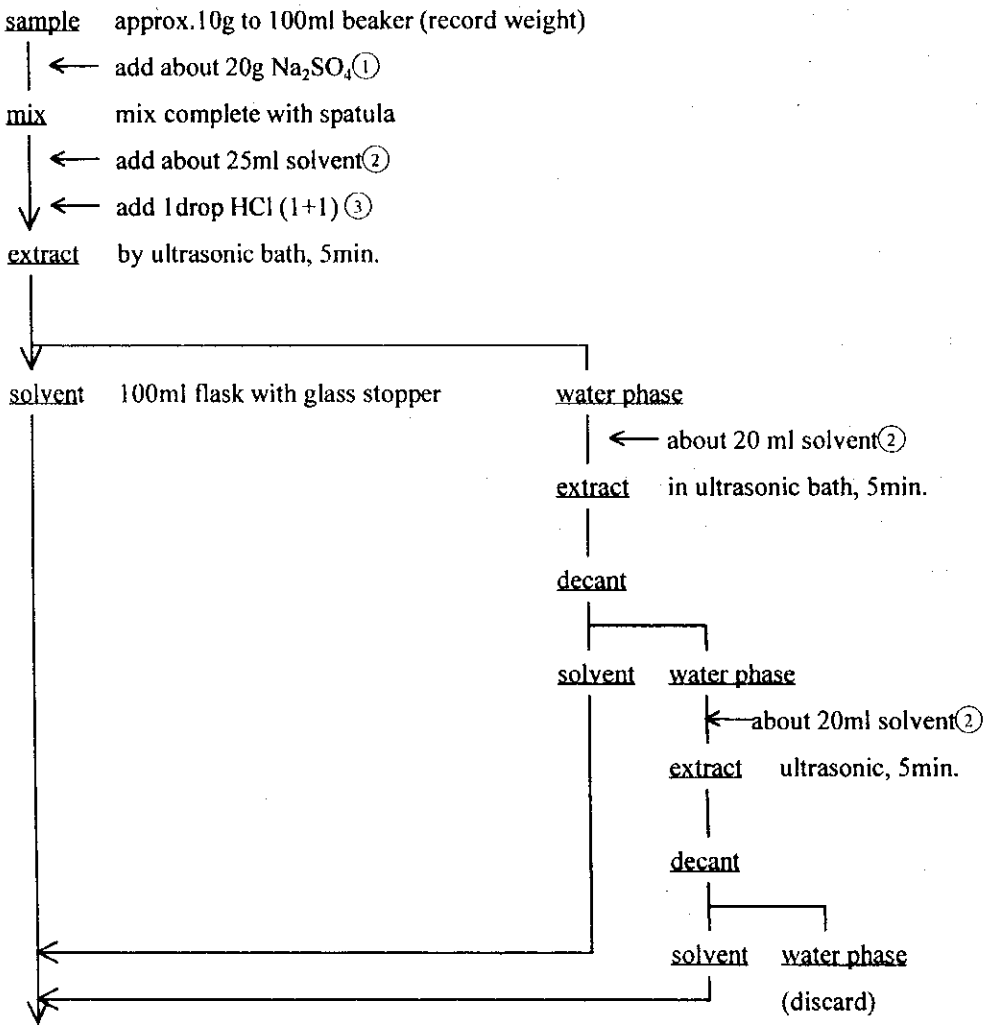
[Apparatus]

- Separating Funnel (1000 ml)
- Filter Paper, Whatman No.40
- Oil Contents Meter (Horiba OCMA300)

[Chemicals]

① Na_2SO_4 (crystal)
② Exclusive Solvent for OCMA300 (CFC-316)
③ HCl(1+1)
④ Silica-gel (60 – 200 mesh)

[Operation Flow]



combine into 100ml flask

↓

fill up with solvent to 70ml

↓ ← add about 3g silica gel ④

stir stirrer, 5min.

↓

filtrate use dry filter paper, separate solvent from silica gel

↓

measure Oil content meter

[calculation]

TPH (ppm) = (a – b) × 2 × 70 / w

Where;

a: concentration shown on Oil Content Meter (mg/L)

b: concentration of blank (mg/L)

2: factor to obtain concentration in solvent

70: solvent volume (ml)

w: taken sample amount (g)

BTEX in Sediment

Gas-chromatographic Method

[Apparatus]

- Vial bottle (20 ml)
- Aluminum cap with PTFE septum
- Ultrasonic Cleaner
- Micro syringe
- GC-FID with Headspace auto-sampler

[Chemicals]

① Sodium Chloride solution, NaCl 30 g → 100 ml of water

② Methanol

③ Mixed reference solution of BTEX

④ Fluorobenzene (1 mg/ml): store in refrigerator

[Operation Flow]

Blank Test
Standards

Preparation of Sample put about 2 g of sediment sample to vial bottle (20 ml)
in advance vial bottle was dried and weighed its tare

↓ Pour NaCl solution① 10 ml, add fluorobenzene (1 mg/ml) ④ 1 µl,
then stopper by aluminum cap with PTFE septum quickly

Extract in ultrasonic cleaner, 10 min.

↓

GC/FID set in headspace auto-sampler

(Blank Sample)

10 ml of NaCl solution①

(Standard Curve)

Working Solution: dilute 1 ml of reference solution to 10 ml with methanol (200 mg/L)
→ store in refrigerator

1) add fluorobenzene (1 mg/ml) 1 µl by micro syringe

2) add 1, 2 and 5 µl of working solution by micro syringe

add volume (µl)	concentration(mg/L)
1	0.02
2	0.04
5	0.10