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GEF GUINEA CURRENT LARGE MARINE ECOSYSTEM PROJECT

SHIP-BOARD TRAINING MANUAL

(A TRAINING MANUAL FOR SHIP-BOARD COASTAL AND MARINE OCEANOGRAPHIC SURVEY AND ASSOCIATED LABORATORY WORK)

MAY, 2005

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INTRODUCTION

1.1 Background:

In response to a request from the United Nations Industrial Development Organization (UNIDO), the Nigerian Institute for Oceanography and Marine Research (NIOMR) has offered to provide services related to the Seaboard/Shipboard Training on Marine Pollution Monitoring Techniques, under the UNIDO Project No. GP/RAF/04/004 defined in the relevant Terms of Reference for scientists in the GCLME region.

1.2 Aims and Objectives

The main objective of this training is to build the capacity of scientists in the GCLME Region to undertake routine marine pollution monitoring for purposes of marine pollution prevention and control.

The aims of the environmental monitoring exercise are as follows:

a) To acquaint participants with practical knowledge on environmental monitoring in the marine environment;

b) To provide ship-board training on physical and chemical oceanographic measurements and sampling procedures at sea:

c) To demonstrate and provide hands-on training on sampling protocol (sample handling, chain of custody, etc.,) and chemical analysis of contaminants and nutrients in seawater;

d) To acquaint participants with knowledge on biological and microbiological sampling for benthos and pathogens respectively;

e) To acquaint participants with methodologies, computation / data analysis and inferences from results.

This manual contains useful notes to meet the foregoing objectives of sea-based and associated laboratory activities.

CHAPTER ONE: SAFETY

Either at sea or in the laboratory, safety is of paramount importance. **As a rule of thumb, no activity should be embarked upon except it is absolutely safe to do so.** The following safety tips are useful and participants should acquaint themselves with this section before any ship-board or laboratory activity:

Part A: Shipboard Activities

Prior to commencement of shipboard activities, hazard evaluation will be carried out along with appropriate education and discussion.

Participants who have no previous sea experience will be given a talk on what to expect at sea

Life jackets must be worn at all times when working on the deck, operating hydrographic winches or deploying sampling gear.

Appropriate coveralls, goggles (where necessary), hand gloves, steel-toe/hard-nosed boots, hard hats etc must be worn at all times especially when working on the deck.

The use of life-raft on the boat for rescue shall be explained and demonstrated to all. So shall readiness in the event of a "Man-overboard" incidence.

Part B Laboratory – based Work

Corrosive chemicals must be handled with care with guidance from laboratory personnel and programme co-ordinators

All are advised to familiarise self with the laboratory floor topography (noting especially differences in elevation) and take precautions against slips, falls and bumps.

Any actions that may result in electrical overloading, shock hazards or fire outbreaks must be avoided. Note locations of nearest fire extinguishers and alternative escape routes.

CHAPTER TWO: GENERAL NOTES ON SAMPLING AT SEA

2.1 Introduction

Marine pollution monitoring involves sea-based and laboratory work. Sea-trips for pollution work usually involve the *in situ* measurements of physical and chemical parameters and the collection of water, sediment and biological samples for subsequent analyses in the laboratory. Essentially therefore, the most important tools are those needed for *in situ* measurements and sample collection for subsequent analysis in the laboratory. There are sampling bottles of various descriptions (and triggering mechanisms) for the collection of water samples while a Grab or Corer is usually employed to collect bottom sediments.

2.2 Useful tips on sea trips

- For any particular trip, there must be clearly defined objectives;
- Based on the objectives, an appropriate and adequately equipped platform (Vessel) can be identified;
- There must be a **cruise plan** to be discussed between the vessel crew and the scientific crew;
- Assemble all necessary equipment and sample containers;
- All equipment must be put through pre – sea trial runs to ascertain functionality;
- Check calibrations where appropriate;
- As much as possible, carry spares for all equipment;
- There must be an accurate positioning system so the data can be geo-referenced (where necessary). Digitized maps of the study area are necessary.
- Safety and security consciousness are important. All safety precautions must be strictly adhered to. If it is not safe, do not attempt any work/activity.

2.3 Nansen Bottles and Reversing Thermometers

The Nansen Bottle / Reversing Thermometer system though becoming old fashioned illustrates a useful mechanism for the collection of water samples and temperature measurement at various depths in the ocean.

The Nansen bottle is a metal sampler with tapered plug valves at both ends. The valves are connected such that both ends of the bottle can be closed or opened simultaneously. The lower end is firmly attached to the wire of an hydrographic winch while the upper end is hooked to the same wire by a tripping mechanism. The bottle is also fitted with a frame for reversing thermometers. There is pressure protected as well as unprotected thermometers. Either also has auxiliary thermometer. The device is lowered into water with the plug valves open so that the bottle is flushed as it is lowered. After leaving the bottles in place at the desired depth for temperature acclimation, a messenger (weight) is attached to the wire and dropped. It triggers the tripping mechanism by disconnecting the top of the bottle from the wire. In the process, the bottle is closed and the attached thermometers are reversed. Where a series of bottles are cast, a second messenger is released which in turn effects the reversal of the next lower bottle until all bottles in the cast have been closed and reversed. The principle of operation of the reversing thermometers is similar to that of a mechanical clinical thermometer. In deep sea casts however, slight changes in temperature may occur but can be compensated for using the combined readings of the protected, unprotected and auxiliary thermometers.

For reasonable profiling of oceanographic parameters, the International Association of Physical Oceanography has proposed standard depths for oceanographic measurements: These depths in meters are: 0, 10, 20, 30, 50, 75, 100, 150, 200, 300, 400, 500, 600, 600, 800, 1,000, 1,200, 1,500, 2,000, 2,500, 3,000, 4,000, 5,000, 6,000.

2.4 CTDs XBTs

In recent times on modern oceanographic vessels, there are devices in which the procedure earlier described have been automated and made amenable to continuous profiling of many parameters *in situ* and the collection of water samples at desired depths. One such device is the CTD assemblage with/without a rosette of samplers. Three sensors permit continuous profiling for conductivity, temperature and depth (as Pressure). The device is first left at the surface for temperature equilibration for a few minutes and then let into the water column. Continuous profile of the three parameters is obtained from the associated computer-ware of the CTD. For the collection of water samples at any desired depth, a sampler can be triggered to close using acoustic signals instead of the messenger used with Nansen bottles.

Where profiling for temperature alone is required, the Expendable Bathythermograph (XBT) can be used. The probe is deployed into the water column using "Guns" designed for the purpose. The probe is connected to the XBT recorder through a thin copper wire. Care should be taken to avoid contact between the copper wire and the body of the ship. As the probe moves down the water column a continuous profile of the temperature with depth is obtained on the XBT recorder.

2.5 Grabs:

Essentially these are devices heavy enough for deep sea operations. They are lowered to the bottom of the sea where the closing mechanism is triggered on impact or by some other means. The collected sediment is then recovered on-board for any desired measurements or analyses.

2.6 Field Sampling for Benthos

Bottom sediments should be collected with a grab sampler (van Veen, Peterson's or Day Grab), $0.1 - 0.5m^2$.

After collection at each station, record details such as depth, colour, texture and the presence of shells. Next empty sample into a plastic bowl and add seawater to dissolve the sediment. Gently stir and carefully sieve through a 0.5mm mesh sieve (McIntyre *et al*, 1984). The content of the sieve after washing is transferred into a properly labeled 1 litre plastic container and 10% formalin (with Rose Bengal stain) added as preservative (Eleftheriou and Holme, 1984). All the time, be careful so that soft bodied invertebrates are not dismembered. The preserved samples should then be kept in boxes for further laboratory analysis.

2.7 Microbiological Sampling

Sampling for micro-biological analysis should ideally be carried out under sterile conditions using specialized gears such as the Niskin sampler and the sterile water sampler described by Jannasch and Maddox (1967). In practice however, and for reasons of logistics and costs, sub-samples for microbiological analysis can also be obtained from the main sample used for other analysis with the important difference that such sub-samples are kept in pre-sterilized containers and stored at low temperatures (refrigeration, freezing or icing). For bottom sediments, obtain sub samples from the main sample, label appropriately and keep at low temperatures until the time for analysis. For water samples, decant directly from water sampler into pre-sterilized and labeled containers. Keep at low temperatures. For biological samples such as fish, obtain samples, label appropriately and keep samples at low temperatures in pre-cleaned containers (such as the commonly available plastic chests) until the time for analysis.

CHAPTER THREE: GENERAL NOTES ON ENVIRONMENTAL QUALITY:

3.1 Water Quality

In practical terms, water quality is definable in terms of the totality of characteristics which a water body should possess to make it suitable for particular purposes for which it may be needed, used directly or abstracted. Water quality is of utmost significance; being consequential for productivity, physiology, health and general wholesomeness of aquatic organisms where the system supports life.

In their pristine form, natural waters usually meet the quality demands of most human uses including suitability as a biological environment. In recent times however, anthropogenic activities, conflicting use demands, cultural and attitudinal practices usually upset the quality of natural waters which is the product over time, of a balance between several natural cycles, interactions and perturbations.

Basically, water quality is determined by a number of factors including the geology of the area of occurrence, inputs of domestic, industrial and agricultural wastes and the prevailing physical (especially mixing) and other related processes. In river systems in particular, for understanding the linkage between the water quality and the sources of natural and man-made inputs, a mass balance of certain water constituents is useful. This basically involves determination of the "Load" of selected substances and the weight of such substance transported through a cross-sectional area in a given period. Changes found in a "Load" along a river can for example point to dilution or to point (discrete) or non-point (diffuse) inputs of pollution not yet identified.

The usual quality parameters and concepts of interest include physical and chemical characteristics, namely:

Temperature
Salinity
Turbidity

Nutrient status

Eutrophication

Dissolved Gases

Dissolved and Suspended Solids

Carbonate Equilibrium

pH (hydrogen ion index)

Phenolic Compounds

Bacteria Load

Load of Toxic Metals

Presence of Agents of water-related diseases

Water flow / Exchange regimes

BOD, COD, Permanganate Value

Biotic Index

Aromatic Hydrocarbons

Polynuclear Aromatic Hydrocarbons

Total Hydrocarbons

Exchangeable cations and anions

Hydrocarbon Utilizers

Total Coliforms

Total Heterotrophic Bacteria

Although there are some common grounds, the magnitude of some of these quality parameters must be within certain ranges in a water medium depending on the use for which it is destined in any particular situation. Outside the respective tolerance ranges, poor growth, ill – health or even death may occur.

Furthermore, any of the foregoing parameters could be limiting: **Temperature** for example could be critical as several metabolic processes occur optimally at particular temperatures while changes in temperature could be signal for some vital physiological activities and can also affect the level of dissolved gases. In the ocean, temperature is one of the critical parameters in the characterization of water bodies.

Salinity is also so significant that some organisms are clearly fresh-water, brackish or marine depending on their innate abilities to deal with the problems of osmotic and ionic regulations so critical for homeostasis irrespective of steno – or euro – halinity.

Temperature and salinity are important tools of characterizing marine waters such that different water bodies can be identified from their characteristic T/S diagrams.

Turbidity is important for light penetration (photosynthetic extent), possible clogging of respiratory surfaces (physical toxicity) and the use of visual organs among others.

Dissolved Oxygen content is critical in natural systems as most organisms have thresholds below which they can not thrive. It is also an important quality index and one of the markers of eutrophication. Good quality water especially as a life support system is generally well oxygenated. Related characterizing and related quality parameters include; BOD. COD DO., NH_4^+ and NO_3^-.

pH - A measure of the acidity or alkalinity of the medium is another important quality parameter. Organisms have pH tolerance ranges outside which they do not thrive while many biochemical, hydrochemical, geochemical and diagenetic processes are pH – dependent.

3.2 Sediment Characteristics

Understanding the nature, distribution and characteristics of bottom sediments is critical in marine environmental monitoring:

Bottom sediments interface with the water medium with possibilities for the exchange of nutrients and contaminants as well. They are also a specialized habitat for a number of marine micro – and macro – infauna. Bottom sediments are also the final sink for several organic, inorganic and detrital materials in the overlying water mass. Thus, cumulative rather than transient information on the dynamics and behaviour of many marine

geochemical marine species can be obtained from appropriate studies on sediment characteristics. The usual quality parameters of interest include:

Texture
Organic content
pH
Redox potential
Exchangeable cations and anions
Organic and inorganic contaminant load.
Poly-nuclear aromatic Hydrocarbons

3.3 Biological components

There are important biological components in the water column and bottom sediments: In the water column, plankton is very important because they are associated with productivity being around the base of the food chain in the sea. The types, distribution density and behaviour should always be known. Also in different strata in the water column are various species of fish. Evaluation of the extent of their contamination is important because it reflects the extent of "cleanliness" of the environment. It also has implications for ecological integrity and consumer safety. Thus, evaluation of the levels of organic and inorganic contaminants in fish and related resources is an important component of any environmental monitoring programme.

The community structure of the benthos is also very important and could be an indication of the contamination or otherwise of the sediments and even the overlying water column. The biological micro-flora in the water, sediment and biological matrices is also usually evaluated in environmental monitoring programmes: The presence or density of public health micro-organisms (coliform bacteria, etc) could serve as early warning signals of danger to human health while the presence of hydrocarbon utilizers could indicate contamination by hydro-carbons.

CHAPTER FOUR: PROCEDURES IN WATER SAMPLING

4.1 Introduction:

Quite often, the need arises to examine a water sample or water body for one or more of the foregoing parameters. In natural water bodies, it is best if the associated measurements can be carried out *in situ*. However, this can only be done with satisfactory precision for a few parameters (e. g. Temperature, Salinity, pH, Dissolved Oxygen) with appropriate care and precautions. For quality control and calibration purposes on these, and for the measurement of other parameters, it is usually necessary to collect WATER SAMPLES on which the desired measurements can then be made.

4.2 Sampling:

Sampling of the water column can be accomplished in a number of ways e. g.

(i) Direct collection into a suitable container using appropriate techniques and taking necessary precautions;

(ii) Lowering of a water sampling device to the desired depth at which a closing mechanism is activated such that a sample at the depth is collected without 'contamination' from other strata while it is brought to the surface.

(iii) Water can be pumped from the depth or area of interest through a hose

In offshore oceanographic work, there are standard depths from which "grab samples" are normally collected.

Whichever way, it is important to maintain sample integrity by:

(i) ensuring that the closing mechanism is reliable and isolates sample completely before it is hauled to the surface.

(ii) Exchange between the surrounding water and that within the sampler should be rapid and total especially in the case of temperature.

(iii) The material of the sampler should not itself be a source of contamination.

There are different types of samplers in use which meet the above criteria.

4.2.1 Sampling under Sterile Conditions.

This is usually done when samples are required for bacteriological purposes. The important thing is that bacteria populations in the sample of interest **must not** be contaminated by those from other sources in the environment or sampling gadgets.

4.3 Filtration:

The need sometimes arises to measure dissolved and particulate components. Separation of the particulate is achievable by centrifugation or, more conveniently, filtration using appropriate filters.

Conventionally in oceanography, material passing through as 0.45um membrane filter is regarded as dissolved. This however is only an operational definition. Filtration can be done at normal pressure or *in vacuo*.

4.4 Storage

Although it is preferable to analyze water samples as soon as possible after collection, there are times when this can not be done and a sample has to be stored. During storage

however, the sample integrity may be undermined (especially with respect to the minor as well as gaseous components). There are also the potential problems of adsorption, contamination and biological changes. These possibilities must be borne in mind and some form of stabilization or "fixation" may be necessary depending on the analysis or examination for which the sample is destined. Appropriate containers which will not contaminate or remove materials from the sample should also be used. Depending on the intended analyses, the samples may be refrigerated after any necessary pre-treatment. In some cases, freezing is sufficient for fixation and preservation. However, although freezing at -10 to 20 ^{o}C is generally effective for many purposes, this in itself may create problems in certain circumstances. It must be pointed out, that even under ideal stabilization and storage conditions, the sample should still be analyzed as soon as possible.

CHAPTER FIVE: PARAMETERS AND GENERAL METHODOLOGIES

Various quality parameters and the methodologies for their measurements are summarized in Table 1.0. The method of choice in a particular situation may depend on intended use of the results, required modesty of accuracy and the medium concerned.

Table 1.0: General Methodologies for Water Quality Parameters

Parameter	General Method
1. 0_2 T°C, pH, Cond/Salinity	Portable Meters, Electronic Probes, Thermometers, Refractometers, Wet Chemistry, CTDs, Salinometers, XBTs, Remote sensing
2. Cl^- PO_4^{3-}, NH_4^+	Field kits, Colorimetry, Standard Methods, Wet Chemistry
3. COD, $No3^-$, $SO4^{2-}$	Sample collection and preservation in the field, Standard Methods, Wet Chemistry, Spectrophotometers,
4. Heavy Metals	Atomic Absorption Spectrophotometry Electrochemistry (eg ASV)
5. Suspended Solids	Gravimetry
7. Turbidity	Secchi Disc. Turbidimeter, Light Meter

5.1 Biotic Index:

The quality of an aquatic environment should be seen not just in terms of the chemistry but in terms of the biology as well. Therefore, while it is useful to establish chemical criteria and indices, biotic indices are also useful. The idea is that certain organisms are associated with certain environmental quality conditions such that their presence or absence indicates the extent of environmental health. Although there are general rules, it is probably a good idea to establish these indices locally for particular areas. Such an index is particularly relevant for low brackish waters fringing marine systems and sometimes seasonally replaced by freshwaters.

CHAPTER SIX: PROTOCOLS ON SPECIFIC METHODOLOGIES

6.1 Water Transparency:

This parameter is usually measured in the field in natural bodies of water.

Materials:

For many practical purposes in natural waters, a Secchi Disc is commonly used. This disc (usually white but sometimes with alternating white and black bands) has a diameter of approximately 30 cm diameter and is sometimes weighted. It may be operated from a winch or just a graduated rope in shallower waters.

Method:

(a) Gently lower the Secchi disc into water on the shadow – side of the boat and note the depth (Z1) at which the disc just disappears;

(b) Raise the disc slowly and note the depth (Z2) at which it just reappears;

(c) Calculate the mean of Z1 + Z2. This gives a measure of water transparency.

6.1.1 Other Methods

Observations on depth of disappearance using a Secchi Disc are only semi – quantitative and may be subjective and dependent on natural variability in visual acuity. It is also clearly irrelevant in people with some form of visual impairment. Besides, they cannot be used before sunrise or after sun set. Less subjective methods involve the use of "Turbidimeters" in which the clarity (transparency) of samples is compared with those of standards (e.g. Formazin) of known transparency.

MATERIALS

-Nephelometer (= Turbidimeter)

-Formazine solution

Procedure :

a) Calibrate Nephelometer with Formazine solution of known NTU (Nephelometric Turbidity Units)

b) Collect water sample in suitable containers (e.g. clean glass vials).

c) Fill Nephelometer curvette and position in the instrument.

d) Measure turbidity by following manufacturer's or instructor's instructions .

e) It is also possible to measure absorption coefficient "Turbidity" by measuring the amount of Light energy incident at the surface and the amounts reaching various depths in the water column.

6.2 Temperature:

MATERIALS

- Insulated Bucket
- Reversing Thermometers mounted on sampling bottles
- Mercury or electronic thermometers
- Multi - parameter probe
- CTDs, XBTs
- Bathythermograph (obsolete)

METHODS:

6.2.1 "Bucket Method"

Method is simple but acceptable for many purposes. Modest accuracy is achievable with necessary precautions.

Sample collection should be preferably done with an insulated bucket and measurement must be made immediately thereafter. Direct sunshine on the bucket must be avoided.

Immerse the thermometer bulb in the bucket sample. Allow about 3 – 4 minutes for thermometer to attain the temperature of the sample (equilibration). Read temperature with thermometer still inside the water sample. Be conscious of and avoid possible errors due to paralfax.

The probe of an electronic thermometer may also be used for measurement from the bucket sample.

6.2.2 Reversing Thermometers:

a) Mount them on reversing sampling bottles.
b) Immerse the latter in water to the required depth.
c) Let thermometers stabilize for 5 minutes before triggering closing mechanism.
d) Pull sampling bottles to the surface and read protected, unprotected and auxiliary thermometers.

6.2.3 Multi-parametric probe:

a) Immerse the probe in water to the required depth
b) Wait for a while until the reading of the probe stabilizes
c) Note the value displayed.

Multi-parametric probes capable of measuring temperature may be used for profiling where the water is shallow enough to accommodate the length of the probe cable.

6.3 Conductivity / Salinity / Temperature

MATERIALS

- Refractometers
- Bottles with screw caps, preferably glass
- Induction Salinometer
- Standard Sea Water (or secondary standard)
- CTDs
- Electronic Probes
- Multi-parametric probes
- Wet Chemistry

6.3.1 Refractometers

1) Callibrate Refractometer with Distilled Water (for 0.00 salinity) or Standard Sea Water (for 35. 0% salinity).
2) Introduce a few drops (one drop is often enough) of sample on the refractive surface of refractometer.
3) Cover sample and read off refractive index which has been scaled as salinity values.

6.3.2 Bench Salinometer

Method

a) Collect water (from sampling bottle) in a clean bottle previously rinsed with distilled water and then with water sample for measurement

b) Put on the screw-cap, seal with parafilm and transport to the laboratory in a cooler at 4°C (with ice bags or cooling packs).

Wrap in aluminium foil (to avoid light) and store in the refrigerator, until analysis (within 24h at most)

d) Remove sample from the refrigerator and let it warm up to room temperature about 25°C) - still wrapped in Aluminium foil.

e) Calibrate Salinometer with Standard Sea water

f) Aspirate sample into measurement cell. If analogue, read off conductivity ratios at null point and check corresponding salinity values from appropriate tables. If digital, read the displayed salinity directly. To prevent the memory effect, rinse cell with distilled water in-between samples.

g) Where applicable, adjust values obtained in the laboratory (e.g. at 25°C) to field temperature conditions by multiplying with appropriate application factors

Complementary *in situ* measurements should be made (for ground truthing) if appropriate field equipment is available, following the manufacturer's instructions.

6.3.3 Electronic kits / Multi-parametric probes

These are simple to use. The manufacturer's instructions and guidance from demonstrators usually suffice. The method basically involves introducing the probe in the sample, making the necessary adjustments and reading off the displayed values.

6.3.4 CTDs

They are particularly useful for vertical profiling for Temperature and Salinity. A suitable vessel fitted with appropriate winch (es) and working platform is necessary.

Select suitable transects sufficient for a three-dimensional picture of distribution pattern. At each station, lower the CTD to just below the water surface and allow about 4 minutes for "acclimation" to the temperature at that depth. Next launch CTD to the intended maximum depth and then hoist back to the vessel.

While descending and or ascending, the vertical distribution of temperature and salinity are recorded by the instrument. Using appropriate programmes (e.g. "SEAS") a three dimensional pattern of the desired distribution can be obtained.

Obtain complimentary *in situ* data at specific depths and locations and depths for ground truthing.

6.3.5 Wet Chemistry

A wet chemical method (Silver Nitrate Titration) is available for salinity determination. It is however obsolescent and will not be demonstrated in this course. It may however be useful for calibration and inter-comparison purposes (Stickland and Parsons, 1965).

6.4 Measurement of pH

MATERIALS

- Field pH- meters
- Laboratory pH- meters
- Thermometers
- Buffers.

METHOD:

a) Collect water (from sampling bottle) in a clean bottle previously rinsed with distilled water and then abundantly with water sample.

b) Close bottle tight and transport to the laboratory in a cooler at 4°C.

c) Store in the refrigerator until analysis (within 6h at most).

d) Before analysis, remove sample from refrigerator and let it warm up to room temperature (about 25°C)

e) Measure pH of water with previously calibrated pH-mete; rinse electrode with distilled water and water sample before each measurement, and immerse for about five minutes before taking readings.

6.5 Dissolved Oxygen (DO)

Concentration of dissolved oxygen can be measured *in situ* (using a mono - or multi-parametric probe) or in the laboratory (by titration).

MATERIAL AND REAGENTS

- Dissolved Oxygen Meter
- Multi-parametric Probe
- Amber glass bottles (300 ml) with glass stoppers
- Automatic Pipettes
- Regular, Semi – automatic or Automatic Burette
- Magnetic Stirrer
- 500ml Erlenmeyer flask
- Manganese Sulphate solution ($MnSO_4.4H_2O$, $MnSO_4.2H_20$, or $MnSO_4, H_20$)
- Sodium or Potassium hydroxide
- Sodium or Potassium iodide
- Sodium azide

- Sodium carbonate
- Concentrated Sulphuric acid (d = 1.84)
- Salicylic acid
- Sodium thiosulphate
- Potassium hydrogen diiodate, $KH(IO_3)_2$
- Potassium fluoride

6.5.1 *IN SITU* MEASUREMENT

a) Calibrate Oxygen meter according to manufacturer's instructions.

b) Immerse the probe in water to the required depth.

c) Read the value displayed (dissolved oxygen) in mg l^{-1} or percentage saturation.

6.5.2 : Azide modification of Winkler's method

This method is in wide use for samples that can not be determined *in situ*. The sample must however be fixed in the field immediately upon collection. Where samples are to be drawn from sampling bottles for various measurements, it is advisable collect sample for DO determination first. Please take all necessary precautions.

The modified Winkler's method using azide has the advantage of eliminating interferences (frequently encountered in conventional Winkler's Operations) due to the photo-sensitivity of iodine, presence of nitrite ions, especially in factory effluents, sewage, river water and in samples incubated for BOD determination.

Preparation of Solutions

i) *Manganese (II) Sulphate Solution (Reagent 1)*

Dissolve 480g $MnSO_4.4H_20$ or 400g $MnCl_2.4H_2O$ or 400g $MnSO_4.2H_20$ or 364 g $MnSO_4.H_20$ in distilled water and make it up to one litre. The solution must not give any color with Starch solution when acidified potassium iodide solution is added.

ii) *Alkaline azido-iodide Solution (Reagent 2)*

a) For more or less saturated samples: Dissolved 500 g NaOH (or 700g KOH) and 135 g NaI (or 150 g KI) in distilled water and make up to one litre. Add 10 g NaN_3 dissolved in 40 ml distilled water. This regent must not give any colour with starch solution when diluted and acidified.

b) For supersaturated samples: Dissolve 10 g of NaN_3 in 500 ml of distilled water. Add 480 g NaOH and 750 g NaI and stir to dissolution. A while precipitate (due to sodium carbonate) will be formed, but should be ignored as it is of no consequence. This solution should not be acidified under any circumstance as toxic fumes of hydrazoic acid may be formed.

(iii) Starch

Dissolve 2 g of soluble laboratory starch and 0.2 g of Salicylic acid in 100 ml boiled distilled water

(iv) Sodium thiosulphate standard solution

Dissolve 6.205 g $Na_2S_20_3.5H_20$ in distilled water. Add 1.5 ml Na0H 6N or 0.4 g solid Na0H and make up to one Litre. Standardise with diiodate solution.

(v) *Potassium hydrogen diiodate standard solution, 0.0021M*

a) Dissolve 812.4 mg $KH(10_3)_2$ in distilled water and make up to 1000 ml

b) Standardization:

Dissolve approximately 2g KI in 100 to 150 ml distilled water. Add 1 ml of 6N H_2SO_4 and 20 ml of the standard diiodate solution. Dilute to 200 ml and titrate the iodine liberated with the sodium thiosulphate solution using starch solution as end point indicator (appearance of pale yellow colour). The volume of sodium thiosuphate (0.025 M) added should be 20 ml at end point.

Method:

a) From the sampling bottle, fill a 300 ml glass amber bottle with water until it over flows, using a PVC tube which delivers the water right at bottom of the bottle.

b) Let water overflow (about 3 times the volume of the bottle) while gently withdrawing the PVC tube to avoid formation of air bubbles.

c) Put on the glass stopper to displace excess water and then remove it again.

d) Quickly pipette 1 ml of Reagent 1 and 1 ml of Reagent 2 to the bottom of the bottle, and cork immediately.

e) Mix by turning the bottle upside down many times. Place it in a closed container (away from light) and transport to the laboratory.

Sample so treated can be stored in darkness (better still under water) for up to one month before analysis.

When ready for analysis;

f) Add 1 ml concentrated H_2S0_4. Recork and mix by turning the bottle upside down several times until the precipitate completely dissolves.

g) Place an aliquot of the mixture (corresponding to 200 ml of original water sample) in an Erlenmeyer flask, after correcting for loss during corking of bottle and addition of reagents. For a total of 2 ml of reagents R1 and R2 used, the volume of mixture to be taken should be 200 x 300/(300 – 2) = 201 ml

h) Carefully mix (on a magnetic stirrer if available) and titrate with 0.025 M solution of $Na_2S_2O_3$ until colour turns pale yellow.

i) Add a few drops of freshly prepared starch solution and continue titrating until the blue colour disappears.

j) Note the volume Vt of thiosulphate used

Calculations of Results:

i) *Expression of results in mg/L*

(Note: The overriding principle is that the relationships are stoichiometric)

According to the equation of the reaction:

1 mole of 0_2 requires 4 moles of $S_20_3^{2-}$

i.e., 32 g of 0_2 → 4 moles of $S_20_3^{2-}$

or 1 g of 0_2 → 1/8 mole of $S_20_3^{2-}$

If V ml of water sample contain X g oxygen.

Xg 0_2 will require x/8 mole of $S_2O_3^{2-}$

But, x/8 mole of $S_2O_3^{2-}$ = Vt (L) x C (mol/1) of $S_2O_3^{2-}$

$$\text{i.e.,} \quad \frac{x}{8} \quad \frac{Vt\ (ml)}{1000} \times C$$

$$x = \frac{Vt\ (ml)}{1000} \times C \times 8$$

If Y is the amount of oxygen (in g) in a litre of sample:

$$Y = \frac{X}{Ve(1)} = \frac{1000.X}{Ve\ (ml)} = 8 \times \frac{Vt(ml)}{Ve(ml)} \times C$$

Dissolved oxygen content in mg/1 is given by:

$$[02]\ mg/1 = \frac{8000 \times Vt \times C}{Ve}$$

Where Vt is volum of sodium thiosulphate solution used for titration of iodine (in ml)

C is concentration of sodium thiosulphate solution (in mol/1)

Ve is volume of sample aliquot (in ml)

For Ve = 200 ml and C = 0.025 M

$$[02]\ mg/l = \frac{8000 \times 0.025 \times Vt}{200} = Vt\ mg/l$$

Dissolved oxygen content (in mg/l) is therefore given by the same number as the volume of $Na_2S_2O_3$ expressed in ml.

Therefore: For Ve = 8.5 ml

[02] = 8.5 mg/l.

ii) *Expression of results in percentage saturation*

$$\% \text{ Sat.} = \frac{[02] \text{ mg/l} \times 100}{C^*}$$

Where % Sat. percentage saturation in oxygen

[02] mg/l: dissolved oxygen content in mg/l

C*: solubility of oxygen in water sample

Solubility C* is related to temperature by the formula;

$$\text{Ln } C^* = -139.34411 + (1.575701 \times 10^5/T) - (6.642308 \times 10^7/T^2) + 1.243800 \times 10^{10}/T^3) - (8.621949 \times 10^{11}/T^4) - \text{chl}\,[(3.1929 \times 10^{-2}) - (1.9428 \times 10/T) + (3.8673 \times 10^3/T^2)]$$

Chlorinity (chl) can be deduced from sample salinity using the formula;

Salinity = 1.80655 x chl

Knowing the temperature and chlorinity, the solubility of oxygen in the water sample can be determined and is obtainable from tables relating Temperature, Chlorinity and Oxygen solubility based on the above formula for C*

Example: Let [02] = 5 mg/l

At 20°C, and for chlorinity of 0.000 mg/l

Ln C* (from table) = 2.207 and C* = 9.092 mg/l

$$\% \text{ Sat} = \frac{5 \times 100}{9.092} = 55.55\ \%$$

At 25°C, and for chlorinity of 10.0 mg/l

Ln C* (from table) = 2.009 and C* = 7.457

$$\% \text{ Sat} = \frac{5 \times 100}{7.457} = 67.05\ \%$$

6.6 Sediment Grading

Information on textural characteristics can be obtained using either the rapid method which broadly separates the silt/clay and sand fractions and or the more rigorous mechanical classification of the sand fraction depending on the required modesty of accuracy or the intended use of the data.

6.6.1 Rapid Analysis

In the rapid method recommended by Buchanan and Kain (1971), an accurately weighed 25 grams of oven dried sediment is dissolved in distilled water containing a sequestrating agents such as Sodium hexametaphosphate or Sodium oxalate. **Please note that complete breakdown of all lumps may take 2 to 3 days**. The sample is then wet-sieved through 63 μm pore size to separate into sand and silt/clay fractions. The fraction retained is dried to constant weight at 80°C. The percentage of the silt/clay fraction is computed from the difference between the weight of the retained fraction and the initial weight of the sediment.

6.6.2 Mechanical Classification of the sand fraction

About 70 to 100g from each air-dried sand fraction sediment sample is passed through a graded series of sieves (2.00, 1.18, 0.60, 0.50, 0.425, 0.25, 0.18, 0.15, 0.125, and 0.063mm) and shaken for 15 minutes on a mechanical shaker (Endecot shaker). The fraction retained on each sieve is weighed and recorded. Next, any remaining organic matter is removed by treatment with 10 % Hydrogen Peroxide and further graded by pipette/sedimentation analysis as outlined by Buchanan and Kain (1971). The corrected settling times for the "Wenthworth grade Scale" are derived from Stoke's law (Appendix II).

6.7 Determination of Total Organic Matter (TOM)

A simple and rapid method for estimating the TOM involves the following procedure: About 10g of sediment is oven-dried to constant weight at 80^0C and placed in a tared crucible. The sample is reweighed before and after ignition in a muffle furnace at 550^0C for 8 hours. The TOM which is also the percentage combustible material is estimated as follows:

$$\frac{\text{Loss in weight on ignition}}{\text{Initial weight before ignition}} \quad X \quad 100\ \%$$

This simple method provides a good estimate of the TOM and has been shown to have a high degree of correlation with methods involving oxidation with sulphuric acid and potassium dichromate (Loring and Rantala, 1977).

6.8. Determination of Heavy Metals in Environmental Samples by Atomic Absorption Spectrophotometry (AAS)

First principles:

AAS is just another application of Beer's law. The normal curvette is replaced by a flame and the sample solution is converted into a gaseous cloud of atoms in the flame. The

monochromatic light beam shoots through the flame rather than the quartz, glass or plastic cuvette which usually contains the solution. In solution UV-vis the electronic transitions taking place involve molecular changes. These molecular electronic transitions have vibrational and rotational spectra superimposed on them. In AAS the molecules are broken down by the flame eliminating any vibrational or rotational spectra. Only gaseous atoms remain in the flame, therefore the spectral peaks in AAS are very sharp, since they come from pure electronic transitions. In AAS the monochromator must have far better resolving power than the monochromators in ordinary UV-vis instrumentation.

You have all seen the color of a Bunsen burner flame when sodium atoms are present. The flame develops a yellow color. The yellow color is a result of electronic transitions taking place in the sodium atoms; however it is not an absorption process. The atoms are excited by the heat of the flame (electrons are promoted into empty orbital). The yellow color is a result of the excited atoms returning to the ground energy state. Flame emission spectrometry is a quantitative technique which makes use of this emitted light. In AAS the electrons are promoted to the excited state by absorption of radiant energy rather than heat energy. At the temperatures in ordinary flames there are far more atoms in the ground state than in the excited state. This means for most elements AAS is the preferred technique rather than flame emission. In order for the radiant energy to be effectively absorbed, the wavelength must correspond exactly to the energy required for the ground state to excited state transition. The energy (and wavelength) is a characteristic property for each element. For each element determined a special light source is required. The light is called a hollow cathode lamp and contains the element being determined, as the cathode in a discharge lamp. AAS is a very selective technique because of the sharpness of the absorption peaks and the uniqueness of the wavelengths for each element.

Concepts, Instrumentation and Techniques

Several related terms are used to define the amount of light absorption which has taken place. The "transmittance" is defined as the ratio of the final intensity to the initial intensity.

$T = I/Io$

Transmittance is an indication of the fraction of initial light which passes through the flame cell to fall on the detector. The ''percent transmission'' is simply the transmittance expressed in percentage terms.

$\%T = 100 \times I/Io$

The ''percent absorption'' is the complement of percent transmission defining the percentage of the initial light intensity which is absorbed in the flame.

$\%A = 100 - \%T$

These terms are easy to visualize on a physical basis. The fourth term, ''absorbance'', is purely a mathematical quantity.

$A = \log (Io/I)$

Absorbance is the most convenient term for characterizing light absorption in absorption spectrophotometry, as this quantity follows a linear relationship with concentration. Beer's Law defines this relationship:

$A = abc$

where ''A'' is the absorbance; ''a'' is the absorption coefficient, a constant which is characteristic of the absorbing species at a specific wavelength; ''b'' is the length of the light path intercepted by the absorption species in the absorption cell; and ''c'' is the concentration of the absorbing species. This equation simply states that the absorbance is directly proportional to the concentration of the absorbing species for a given set of instrumental conditions. This directly proportional behavior between absorbance and concentration is observed in atomic absorption. When the absorbances of standard solutions containing known concentrations of analyte are measured and the absorbance data are plotted against concentration, over the region where the Beer's Law relationship is observed, the calibration yields a straight line. As the

concentration and absorbance increase, non ideal behavior in the absorption process can cause a deviation from linearity.

After such a calibration is established, the absorbance of solutions of unknown concentrations may be measured and the concentration determined from the calibration curve. In modern instrumentation, the calibration can be made within the instrument to provide a direct readout of unknown concentrations. Since the advent of microcomputers, accurate calibration, even in the nonlinear region, is simple.

THE BASIC COMPONENTS

To understand the workings of the atomic absorption spectrometer, let us build one piece by piece. Every absorption spectrometer must have components which fulfill the three basic requirements. (1) a light source; (2) a sample cell; and (3) a means of specific light measurement.

The most widely used source is the hollow cathode lamp. These lamps are designed to emit the atomic spectrum of a particular element, and specific lamps are selected for use depending on the element to be determined.

Special considerations are also required for a sample cell for atomic absorption. An atomic vapor must be generated in the light beam from the source. This is generally accomplished by introducing the sample into a burner system or electrically heated furnace aligned in the optical path of the spectrophotometer.

The portion of an atomic absorption spectrometer's optical system which conveys the light from the source to the monochromator is referred to as the *photometer*.

Pre-Mix Burner System

The sample cell, or atomizer, of the spectrometer must produce the ground state atoms necessary for atomic absorption to occur. This involves the application of thermal energy

to break the bonds that hold atoms together as molecules. While there are several alternatives, the most routine and widely applied sample atomizer is the flame.

The Burner system consists of the burner head, burner mixing chamber, flow spoiler, end cap, nebulizer, and drain. The nature of the aspirated samples determines how often you have to clean the burner system. The burner should provide an even flame over the length of the slot.

The Stand-alone Computer and Atomic Absorption

Stand-alone and personal computers have extended the automation and data handling capabilities of atomic absorption even further. These computers can interface directly to instrument output ports to receive, manipulate, and store data and print reports in user selectable formats. Also, data files stored in personal computers can be read into supplemental software supplied with the system or third party software such as word processor, spreadsheet and database programs for open-ended customization of data treatment and reporting.

NONSPECTRAL INTERFERENCES

Interferences in atomic absorption can be divided into two general categories, spectral and nonspectral. Nonspectral interferences are those which affect the formation of analyt atoms.

Matrix Interference

The first place in the flame atomization process subject to interference is the very first step, the nebulization. If the sample is more viscous or has considerably different surface tension characteristics than the standard, the sample uptake rate or nebulization efficiency may be different between sample and standard. If samples and standards are not introduced into the process at the same rate, it is obvious that the number of atoms in the light beam and, therefore, the absorbance, will not correlate between the two.

Chemical Interference

A second place where interference can enter into the flame process is in the atomization process. In this step, sufficient energy must be available to dissociate the molecular form of the analyte to create free atoms. If the sample contains a component which forms a thermally stable compound with the analyte that is not completely decomposed by the energy available in the flame, a chemical interference will exist.

Ionization Interference

There is a third major interference, however, which is often encountered in hot flames. The dissociation process does not necessarily stop at the ground state atom. If additional energy is applied, the ground state atom can be thermally raised to the excited state or an electron may be totally removed from the atom, creating an ion. As these electronic rearrangements deplete the number of ground state atoms available for light absorption, atomic absorption at the resonance wavelength is reduced. When an excess of energy reduces the population of ground state atoms, ionization interference exists.

SPECTRAL INTERFERENCES

Spectral interferences are those in which the measured light absorption is erroneously high due to absorption by a species other than the analyte element. The most common type of spectral interference in atomic absorption is "background absorption."

Background Absorption

Background absorption arises from the fact that not the entire matrix materials in a sample are necessarily 100 % atomized. Since atoms have extremely narrow absorption lines, there are few problems involving interferences where one element absorbs at the wavelength of another. Even when an absorbing wavelength of another element falls within the spectral bandwidth used, no absorption can occur unless the light source produces light at that wavelength, i.e., that element is also present in the light source.

PREPARATION OF SAMPLES FOR AAS ANALYSIS

Equipment

1. Beakers
2. Volumetric Flasks 25 ml, 50 ml
3. Hot plate
4. Filter Paper
5. Deionised Water
6. Dissecting Set
7. Pistil and Mortar

Aqua regia extraction acid

1) in 400 ml cylinder, add

- 300 ml concentrated HCl
- 100 ml concentrated HNO3

2) transfer to 1000 ml volumetric

3) bring to volume with diH2O

4) invert to mix; allow to stand; recheck volume

Nitric/Hydrogen Peroxide (30%)

1) in 500 ml cylinder

- 200 ml HNO_3
- 200 ml H_2O_2

2) invert to mix; allow to stand.

Procedure for Sediment and Fish Tissue

1) Dry sediment sample at 70 °C, for 24 hours

2) Grind sample in a mortar

3) Wash beakers in 10 % HNO3 and dry in oven for 2 hours.

4) Label beakers adequately

5) Weigh out ~0.5000 g of sediment and 10 g of fish tissue, ground sample into each beaker using Mettler (four-place) balance. Record sample code and weight.

6) Add to each 250 ml beaker containing the sample 100 ml H_2O_2/HNO_3 or

Aqua regia extracting acid. Cover the beaker with a watch glass and set aside for about 1 hour for the initial reactions to subside.

7) The beaker and the contents were placed on a hot plate, whose temperature was allowed to rise gradually, but not exceeding 160 ^{o} C in a fume cupboard. Heating should continue for about 2 hours, reducing the volume in the beaker to 2 ml. This digestion procedure is repeated twice.

8) The beaker and its contents were allowed to cool and the contents transferred to a 25 ml volumetric flask by filtration and made up to the mark by distilled water.

9) Prepare reagent blanks accordingly to determine the purity of the reagents.

10) Consult the detailed atomic absorption method for each particular analyte. Determine the linear range of concentrations for the wavelength to be used and devise an appropriate sample dilution scheme.

11) Measure diluted extract by Atomic Absorption Spectrophotometry. Calculate dry sample content from measured dilute extract value.

11) As recovery check, digest if possible certified reference material in parallel to unknowns.

6.9 Nutrients Determination

6.9.1. Phosphate

Natural unaffected waters mostly contain total phosphorus compounds at concentrations of less than 0.1 mg/l. Phosphorus compounds are fixed in the soil to such an extent that the danger of seepage to the deeper layers or even into the groundwater is relatively slight. However, surface waters can have significant phosphorus concentrations caused by soil erosion, agricultural runoffs, and effluent introduction.

Determination[1]

Phosphate is determined as orthophosphate with ascorbic acid spectrophotometric procedure. In acid solution, phosphate and molybdate form a complex, which is reduced by ascorbic acid to give to a blue colour of intensity proportional to the phosphate ions. A standard calibration curve is obtained by preparing phosphate solutions using KH_2PO_4 dried in the oven at 105 ^{o}C for 1 hour. 8 ml of the reducing reagent (mixture of ammonium molybdate, potassium antimonyl tartarate, sulphuric acid and ascorbic acid) is added to 50 ml of each of the standard solutions. The absorbance of the molybdenum blue colour is measured at 880nm with a spectrophotometer. The blue colour is developed for 25 minutes in each case.

Sample Determination

50 ml of filtered sample shall be used in each case. 8ml of the reducing reagent is added and the colour developed for 25 minutes and the absorbance of the molybdenum blue

measured with the same spectrophotometer at 880 nm. A blank sample is measured in the same way.

6.9.2. Nitrate

Nitrate is found in many natural waters at concentrations between 1 and 10 mg/L. Higher concentrations often indicate the effects of nitrogen-containing fertilizers since the NO_3^- ion is badly adsorbed in the soil and so easily finds its way into the groundwater. Very high nitrate concentrations are normally encountered in treated waste waters, a result of ammonium nitrogen being totally or partially oxidized to nitrate by microbial actions. On the other hand, ammonium dominates in raw waste water.

The parameter is of great importance in assessing the self-purification properties of water systems and the nutrient balance in surface waters and soil.

Determination.[1]

The phenoldisulphonic acid spectrophotometric method is used for the determination of nitrate. The yellow colour produced by the reaction between nitrate and henoldisulphonic acid obeys Beer's law up to at least 12 mgN/l at a wavelength of 480 nm when a light path of 1 cm is used. At a wavelength of 410 nm, the point of maximum absorption, determinations may be made up to 2 mg/l with the same cell path. A calibration curve is obtained by preparing standard solutions using KNO_3 dried in the oven 105 ^{o}C for 1hour. Calibration standards are prepared by taking the appropriate aliquots of the stock nitrate into 50 ml standard flasks and diluted to mark with distilled water. Each of these is then evaporated to dryness on a clean porcelain-evaporating dish on a water bath. The residue

is rubbed with 2 ml of phenoldisulphonic acid reagent and the yellow colour is developed with 6-10 ml concentrated ammonium hydroxide solution in a 50 ml volumetric flask which is made up to mark with distilled water. The absorbance of the yellow colour developed is measured at 410 nm with a Spectrophotometer.

Sample Determination

The samples are treated as follows: 50 ml of filtered raw water sample is measured into porcelain evaporating dish, and the equivalent millilitre of standard Ag_2SO_4 is added to mask the chloride ions which may otherwise interfere. The AgCl formed is coagulated by heating on a water bath and the precipitate filtered off. The resulting filtrate is quantitatively transferred back into the evaporating dish and evaporated to dryness on a water bath. 2 ml of the phenoldisulphonic acid is used to rub the residue, diluted with 20 ml of distilled water and the yellow colour developed with concentrated ammonium hydroxide. The absorbance is measured at 410 nm with the same Spectrophotometer as for standards. The nitrate concentration is obtained from the calibration curve. A blank sample is measured in the same way.

6.9.3 Nitrite

Nitrite ions are found in unpolluted waters at levels not exceeding 1 µg/l. The ion can occur at greater concentrations as an unstable intermediate during nitrification of ammonium, especially where toxic effects are detected. It can be toxic to certain aquatic organisms at concentrations under 1 mg/l. Its presence is not permissible in drinking water.

Determination[2]: In the presence of hydrochloric acid and N-(1-naphthyl)-ethylenediamine-dihydrochloride, sulphanilamide reacts with nitrites to give a pink colour proportional to nitrite concentration.

Apparatus: Spectrophotometer (540nm).

Reagents and Solutions

0.5 g sulphanilamide and 0.05 g N-(1-naphthyl)-ethylenediamine-dihydrochloride is dissolved in 25 ml distilled water and 10.5 ml 36 % HCl. 13.6 g sodium acetate trihydrate is added and the solution made up to 50 ml. The solution is stable for several months.

Nitrite Standard Solution (1000 mg/l, 1 mg/l)

1.500 g sodium nitrite (dried for 1 hour at 105 °C) is made to 1L with distilled water. The solution is stable for approx. one month at 4 °C. 1ml of this solution is made up to 1L with distilled water.

Sample Preparation

The analysis should be carried out within few hours of sample collection. In all cases, the sample must be kept cool until examination. Discolouration and colloidal turbidity may be removed by aluminium hydroxide flocculation. At pH > 10 or base capacity exceeding 6 mmol/L, the pH value is adjusted to pH 6 with dilute hydrochloric acid.

Calibration and Measurement

The standard curve is prepared as follows: 1 to 25 ml of the diluted nitrite standard solution are pipetted into 50 ml graduated flasks, diluted to approx. 40 ml and 2 ml reagent solution are added. The flasks are filled, the content mixed and measured at 540 nm after leaving for 15mins. The pH should lie between 1.5 and 2. A blank sample is measured in an identical manner.

Interfering Factors

Nitrogen-oxides possibly present in the laboratory air can interfere with the determination. Strong oxidizing and reducing agents (active chlorine, sulphites) at high concentrations can also interfere.

Calculation of Results

The nitrite concentration is calculated by reference to the calibration curve and blank value obtained.

6.9.4. Silicate.

Silicon occurs as one of the most abundant elements in all rocks and sediments. Silicon compounds such as silicates can be dissolved from such materials by weathering processes and so reach the water cycle. Silicates can be found in dissolved, colloidal or suspended form. The concentration in natural waters lies usually in the range from 0 – 20 mg/L but higher concentrations can be found in some strongly mineralized waters. Silicate is an undesirable component in waters for industrial use as deposits can be formed in pipes or boilers.

Determination[2]

Apparatus: Spectrophotometer (812 or 650 nm)

Reagents and Solutions

Ammonium molybdate solution: 10 g ammonium molybdate.tetrahydrate is made up to 100 ml with warm distilled water. After filtration and adjustment of pH to 7, the solution is stored in a plastic bottle.

Oxalic Acid: 10 g of oxalic acid .dihydrate is made up to 100 ml with distilled water.

Hydrochloric Acid 20 %.

Sodium carbonate solution: 25 g of anhydrous sodium carbonate is dissolved in 1L distilled water.

Silicic Acid standard solution (10 ml/L): A ready-made standard solution in ampoules is used. Where these are not available, standards should be prepared as follows:

1 g of silicon dioxide is heated in a platinum crucible for approx. 1hour at 1100 °C. After cooling, 5 g of anhydrous sodium carbonate is added. The mixture is heated until it melts. Splashes must be avoided. After cessation of gas development, heating is continued at light red-hot temperature for approx. 10 mins. On cooling, the melt is dissolved in distilled water, and made up to 1L. The solution is stored in plastic bottle. It contains 1000 mg/l SiO_2. 10 ml of this solution are taken and made up to 1L.

Sample Preparation

Before determination of the dissolved Silicic acid, the sample is passed through a 0.45 um membrane filter. If the colloidal Silicic acid is also to be determined, the sample must be dissociated: 100 ml of sample are placed in a platinum crucible together with 20 ml sodium carbonate solution, and carefully evaporated down to 80 ml. This solution is transferred to a 100 ml volumetric flask. 5 ml hydrochloric acid (20 %) is added and the flask topped.

Calibration and Measurement

1 to 10 ml aliquots of the Silicic acid standard solution are taken and made up to 50 ml. These solutions are measured together with 50 ml of sample by adding 1 ml of hydrochloric acid (20 %) and 2 ml of ammonium molybdate. After mixing, 1.5 ml of oxalic acid solution is added and mixing is continued. After 5 mins, measurement is carried out at 812 or 650 nm.

Owing to the lower sensitivity at 650 nm, 0 to 30 ml of standard should be used to construct the calibration curve. A blank is treated in the same way as the sample.

Interfering Factors

Phosphate, Iron and Sulphides can interfere. Interference by phosphate is reduced by addition of oxalic acid. Colour interference can be compensated by photometric comparison measurements.

Calculation of Results

The content of Silicic acid is obtained by reference to the calibration curve.

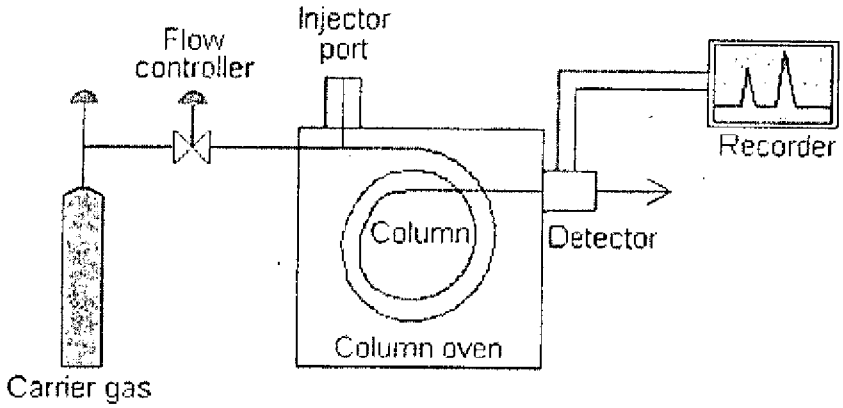
6.10 Determination of Hydrocarbons, PCBs and PAHs in Environmental Matrices

6.10.1 Introduction to Gas Chromaography

Gas chromatography - specifically gas-liquid chromatography - involves a sample being vapourised and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column

itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid.

Have a look at this schematic diagram of a gas chromatograph:



6.10.1.1 Instrumental components

6.10.1.1.1 Carrier gas

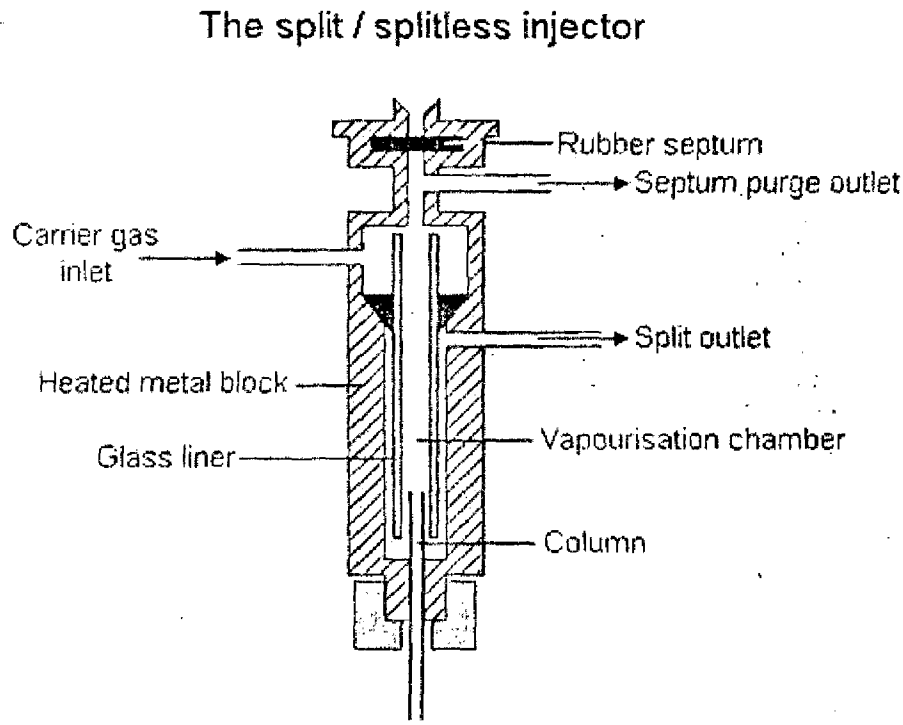
The carrier gas must be chemically inert. Commonly used gases for this purpose include nitrogen; helium, argon, and carbon dioxide. The choice of carrier gas is often dependant upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities.

6.10.1.1.2 Sample injection port

For optimum column efficiency, the sample should not be too large, and should be introduced into the column as a "plug" of vapour - slow injection of large samples causes band broadening and loss of resolution. The most common injection method is where a microsyringe is used to inject sample through a rubber septum into a flash vapouriser port at the head of the column. The temperature of the sample port is usually about 50 °C

higher than the boiling point of the least volatile component of the sample. For packed columns, sample size ranges from tenths of a microliter up to 20 microliters.

Capillary columns, on the other hand, need much less sample, typically around 10^{-3} µL. For capillary GC, split/splitless injection is used. Have a look at this diagram of a split/splitless injector;



The injector can be used in one of two modes; split or splitless. The injector contains a heated chamber containing a glass liner into which the sample is injected through the septum. The carrier gas enters the chamber and can leave by three routes (when the injector is in split mode). The sample vapourises to form a mixture of carrier gas, vapourised solvent and vapourised solutes. A proportion of this mixture passes onto the column, but most exit through the split outlet. The septum purge outlet prevents septum bleed components from entering the column.

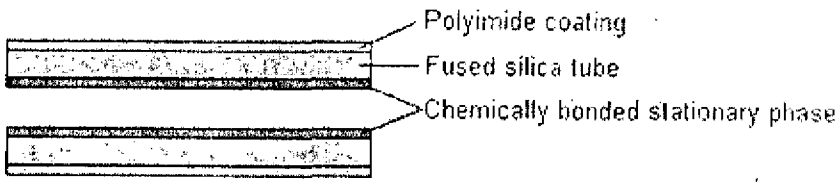
6.10.1.1.3 Columns

There are two general types of column, *packed* and *capillary* (also known as *open tubular*). Packed columns contain a finely divided, inert, solid support material (commonly based on *diatomaceous earth*) coated with liquid stationary phase. Most packed columns are 1.5 - 10m in length and have an internal diameter of 2 – 4 mm.

Capillary columns have an internal diameter of a few tenths of a millimeter. They can be one of two types; *wall-coated open tubular* (WCOT) or *support-coated open tubular* (SCOT). Wall-coated columns consist of a capillary tube whose walls are coated with liquid stationary phase. In support-coated columns, the inner wall of the capillary is lined with a thin layer of support material such as diatomaceous earth, onto which the stationary phase has been adsorbed. SCOT columns are generally less efficient than WCOT columns. Both types of capillary column are more efficient than packed columns.

In 1979, a new type of WCOT column was devised - the *Fused Silica Open Tubular* (FSOT) column;

Cross section of a Fused Silica Open Tubular Column



These have much thinner walls than the glass capillary columns, and are given strength by the polyimide coating. These columns are flexible and can be wound into coils. They have the advantages of physical strength, flexibility and low reactivity.

Column temperature

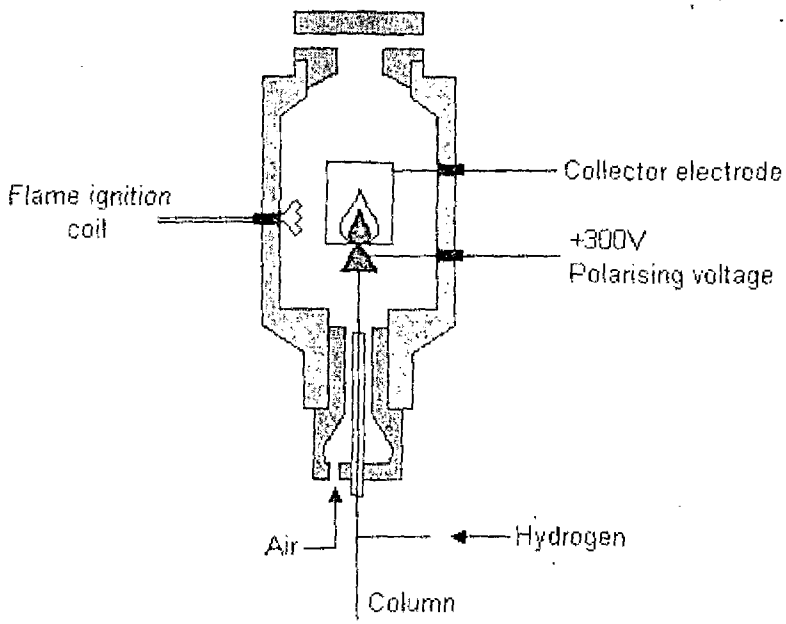
For precise work, column temperature must be controlled to within tenths of a degree. The optimum column temperature is dependant upon the boiling point of the sample. As a rule of thumb, a temperature slightly above the average boiling point of the sample results in an elution time of 2 - 30 minutes. Minimal temperatures give good resolution, but increase elution times. If a sample has a wide boiling range, then temperature programming can be useful. The column temperature is increased (either continuously or in steps) as separation proceeds.

6.10.1.1.4 Detectors

There are many detectors which can be used in gas chromatography. Different detectors will give different types of selectivity. A *non-selective* detector responds to all compounds except the carrier gas, a *selective detector* responds to a range of compounds with a common physical or chemical property and a *specific detector* responds to a single chemical compound. Detectors can also be grouped into *concentration dependant detectors* and *mass flow dependant detectors*. The signal from a concentration dependant detector is related to the concentration of solute in the detector, and does not usually destroy the sample Dilution of with make-up gas will lower the detectors response. Mass flow dependant detectors usually destroy the sample, and the signal is related to the rate at which solute molecules enter the detector. The response of a mass flow dependant detector is unaffected by make-up gas. Have a look at this tabular summary of common GC detectors:

Detector	Type	Support gases	Selectivity	Detectability	Dynamic range
Flame ionization (FID)	Mass flow	Hydrogen and air	Most organic cpds.	100 pg	10^7
Thermal conductivity (TCD)	Concentration	Reference	Universal	1 ng	10^7
Electron capture (ECD)	Concentration	Make-up	Halides, nitrates, nitriles, peroxides, anhydrides, organometallics	50 fg	10^5
Nitrogen-phosphorus	Mass flow	Hydrogen and air	Nitrogen, phosphorus	10 pg	10^6
Flame photometric (FPD)	Mass flow	Hydrogen and air possibly oxygen	Sulphur, phosphorus, tin, boron, arsenic, germanium, selenium, chromium	100 pg	10^3
Photo-ionization (PID)	Concentration	Make-up	Aliphatics, aromatics, ketones, esters, aldehydes, amines, heterocyclics, organosulphurs, some organometallics	pg	10^7
Hall electrolytic conductivity	Mass flow	Hydrogen, oxygen	Halide, nitrogen, nitrosamine, sulphur		

The Flame Ionisation Detector



The effluent from the column is mixed with hydrogen and air, and ignited. Organic compounds burning in the flame produce ions and electrons which can conduct electricity through the flame. A large electrical potential is applied at the burner tip, and a collector electrode is located above the flame. The current resulting from the pyrolysis of any organic compounds is measured. FIDs are mass sensitive rather than concentration sensitive; this gives the advantage that changes in mobile phase flow rate do not affect the detector's response. The FID is a useful general detector for the analysis of organic compounds; it has high sensitivity, a large linear response range, and low noise. It is also robust and easy to use, but unfortunately, it destroys the sample.

6.10.2 ANALYZING SEMIVOLATILE ORGANIC COMPOUNDS

6.10.2.1 Introduction

These analyses are some of the most common tests performed by environmental laboratories, yet there are many analytical challenges of which the analyst needs to be aware. For example, the samples often are highly contaminated with non-target compounds (e.g., hydrocarbons) and so, quality assurance/control (QA/QC) of the methods must be rigorous. There are a number of procedures and techniques that can be employed, however, to make these analyses simpler to perform. The following notes are useful.

6.10.2.2 Extraction

The compounds of interest may be difficult to extract because they fall into different chemical classes (i.e., acidic, basic, neutral, halogenated, oxygenated, polar, non-polar, low-boiling, and high-boiling compounds). Therefore the method will need to solvate a wide variety of compounds. It must also recover the analytes of interest while removing the interfering non-target contaminants. This limits the choices of cleanup options. A number of sample extraction methods can be applied to these compounds, but only the most common will be addressed in the manual.

6.10.2.2.1 Liquid Samples

For liquid samples, either separatory funnel extraction or automated liquid-liquid extraction may be used. Separatory funnel extraction is faster and less expensive to set up than the other methods, but it requires continuous operator attention. Automated liquid-liquid extractors run unattended, but are more expensive and, if analyte recovery is lower than allowed, re-extraction by separatory funnel may be required. Alternatively, if the sample forms an emulsion to the degree that acceptable solvent recovery is not possible using a separatory funnel, then some samples, will require automated liquid-liquid extraction. Solid phase extraction is an alternative for aqueous samples.

For **Separatory Funnel Extraction**, measure up to 1 L of water into a 2 L separatory funnel and adjust to pH >11 using 10 M NaOH; be careful not to add too much base. Then extract the sample by adding 60mL of dichloromethane and shaking for 2 minutes.. It is critical to shake all samples consistently or variations in extraction efficiency will be observed. The best way to ensure consistency is to use a mechanical separatory funnel shaker, as there often is considerable variation with manual extractions. Allow the dichloromethane layer to settle to the bottom of the funnel and then decant that layer into a collection vessel (e.g., rotary evaporator). This extraction method is repeated twice more to get quantitative recovery of all analytes. Collect all the three extractions into the same collection vessel and label as base/neutral.

Then adjust the water sample to a pH of slightly less than 2 using sulfuric acid. (1:1, v/v). Avoid over acidification because I can result in acidic extract. Repeat extraction on the water sample as described above, collecting extracts in separate collecting vessel and labeling it as acid fraction.

It is critical to remove water from the dichloromethane before you concentrate the extract to final volume. Dichloromethane can hold approximately 11ml of water per liter of solvent. If this water remains, it will partition out when the volume is reduced. This will result in dichloromethane boiling of first, leaving water in the collection vessel, and the formation of two-layer extract. The analyte recoveries will b lower than desired, and the presence of water will interfere with the GC analysis. The optimum way to remove the water is to decant the dichloromethane through granular sodium sulfate, which is held in a funnel with a high quality grade filter paper (e.g., Whatman 541). Approximately 30 g of sodium sulfate are sufficient for most samples.

Automated liquid-liquid extraction can run unattended once the samples are ready and the solvent is added. This extraction is performed at a single pH to 2, but some methods can call adjusting the pH to 4. In any event it is critical not to allow the pH goes below 2 when using a liquid-liquid extractor. If this happens an acidic extract will form and may cause damage to the GC column. Acidic extracts also will cause low recoveries for the late eluting internal standards, possible due to isotopic exchange (e.g., perylene-d12).

Automated liquid-liquid extractors are available in two versions-conventional and accelerated. The conventional types use 1 L of swampland extract using 100 to 500 ml of dichloromethane. These extraction vessels are typically operated for 16 to 24 hours in order to achieve complete extraction. The accelerated extractor uses a hydrophobic membrane to separate the aqueous from the organic phase and the extraction time can be reduced by 25 % to 30 % compared to conventional extractor. However, the membranes are expensive.

Finally, **solid phase extraction** (SPE) also may be used to extract semi-volatile organic compounds from aqueous samples. When using SPE, it is extremely important to follow the manufacturer's recommendations for product use. There are several manufacturers of C18 cartridges and disks, which are the typical media for the compounds. The specific steps to extract these compounds will vary somewhat depending on the manufacturer. One of the biggest problems with SPE is plugging of the disk or tube with suspended solids, so this method only works reliably for drinking water samples. If contamination levels are low and the samples are free of solids, SPE provides very fast extraction times and low solvent usage. It is used easily for field extractions.

6.10.2.2.2 Soil Samples

Soxhlet and ultrasonic extraction are the most common techniques for solid samples; although pressurized fluid, microwave and supercritical fluid extraction (SFE) also can be used.

Because the soil and biota samples essentially are wet samples, acetone and dichloromethane (1:1) are usually used as extraction solvent. Acetone is needed to adequately penetrate the soil particle so that compounds in the particle can be extracted.

All solvents used for extraction must be pesticide-residue grade, and a solvent assay should be performed to verify purity before use. To perform a solvent assay, evaporate 300 ml to 400 ml of solvent to a final volume of 1ml and analysed by GC/MS the

resulting chromatogram should have no compounds quantitated above ½ the detection limit for any target compound.

Soxhlet and ultrasonic extraction work well for the semi-volatile compounds. Sonication is a faster technique but requires constant operator attention. In both techniques problems are usually caused by contaminated reagents (especially sodium sulfate) or by inconsistent handling from sample to sample. Sodium sulfate must be treated to remove water and sample must be mixed with the Sodium sulfate to achieve a sandy consistency.

Pressurized fluid extraction (=Accelerated solvent Extraction) can be run in an unattended fashion with multiple samples across a wide sample size range. Extraction vessels with volumes of 1 to 100 ml are available. Instruments like the Dionex ASE 200 accommodate wet samples from 1 to 15 grams, and the Dionex ASE 300 will accommodate wet samples from 15 to 50 grams. The volume of the cell needed for wet samples is generally twice the gram weight of the sample being used. For example, if 30-g wet samples are needed, the 66-ml and 100-ml vessels will be adequate for these extractions. This is necessary because a drying agent such as diatomaceous earth is added to the sample prior to being loaded into the extraction vessels.

Microwave extraction can be useful for automated extraction as well. This method typically performs the extraction of 12 samples at the same time, but requires more operator handing than the pressurized fluid extraction instruments. Microwave extraction instrumentation is less expensive and saves time and solvent, but can suffer from the same sample size limitations.

6.10.2.3 CLEANUP

Sample extract cleanup may be the most important step in maintaining long-term instrument performance. Many times when instrument problem arise, they are caused by exposure of the injection port and the column to material in the sample extracts other than the target compounds. While all contaminants cannot be eliminated, reducing them will

minimize injection port and column maintenance. Most semi-volatile extracts, especially those extracts from soil and biota samples, contain high-boiling hydrocarbons and lipids.

The difficulty in attempting to remove them using one of the common solid-liquid cleanup techniques (e.g., florosil and silica gel) is that the cleanup technique removes some of the target compounds. In addition, because the analytical method usually calls for reporting of several tentatively identified compounds (TICs), it is not desirable to clean the extracts of compounds that would normally elute in the range of the target compounds. For theses reasons, get permeation chromatography (GPC) is the only universal cleanup technique for semi-volatile extracts.

6.10.2.3.1 Gel Permeation Chromatography.

Gel Permeation Chromatography (GPC) is a preparative scale chromatographic method of separation based on molecular size. Because the target compounds are similar in molecular size, they elute as band of material and are easily separated from lighter and heavier contaminants. However, GPC systems are expensive and the processing time per sample is between 30-70 minutes. For these reasons many laboratories choose not to use GPC. However, it is very efficient for removing sulfur, high molecular weight hydrocarbons and lipids from semi-volatile extracts; and may be prudent for soil and biota samples. In spite of the added expense and time required for GPC it is best alternative for extract cleanup.

6.10.2.3.2 Ready-packed Clean-up Cartridges

Factory packed clean-up chromatographic columns are available. They are usually method dependent; the method itself dependent on the analyte(s) of interest and the solvent regimes employed. For example, in the USA EPA methods compendium, factory-

prepared silica cartridge cleaning chromatographic columns are available for PCBs and PAHs under methods bearing appropriate code numbers.

6.10.2.4 Analysis

Calibration standards are purchased as mixtures and usually are divided among three to seven separate ampoules due to the cross-reactivity of several compounds.

On column injection technique can eliminate breakdown or adsorption in the injection system and improve chromatographic analysis for drinking water extracts or extracts with little or no non volatile residues. We do not recommend on-column injections for soil and biota extracts that contain large amounts of non-volatile residue, because the analytical column can be contaminated quickly.

To reduce solvent peak tailing, splitless injection is most commonly used for GC/MS analysis of semi-volatile compounds.

The total analysis time should be as short as possible without sacrificing separation or resolution between compounds with similar mass spectra.

6.11 Determination of bacteria loadings in environmental matrices

6.11.1 Benthic/surface water Microbiology Sample Collection

Bottom sediment samples are collected from grab samples with appropriate and pre-strerilised utensils. Water samples are collected aseptically in sterile containers. In either case, the samples are packed and transported to the laboratory in ice and analysed within 3-6 hours.

6.11.2 Hydrogen Utilizing Bacteria

Hydrogen bacteria oxidize hydrogen gas (H_2) as an energy source. The hydrogen bacteria are facultative lithotrophs as exemplified by the pseudomonads that possess a hydrogenase enzyme that will oxidize H_2. They will use H_2 if they find it in their environment even though they are typically heterotrophic. Most hydrogen bacteria are nutritionally – versatile in their ability to use a wide range of carbon and energy sources (Todar, 2004).

6.11.2.1 Microbiological analysis

Ten fold serial dilution of soil is prepared and cultures obtained by plating on nutrient agar incubated at 28 to 2°C for 24-48 hours. Solates are identified using morphological and biochemical characteristics (Sneath, 1966).

6.11.2.2 Total Heterotrophic Bacteria

Heterotrophic bacteria are masters of decomposition and biodegradation in the environment. They use organic compounds as sources for generating cellular energy and as the source of carbon for incorporating into cellular structures. The respiratory and fermentative metabolisms of heterotrophic organisms return inorganic Carbon-dioxide to the atmospheric.

6.11.2.2.1 Microbiological analysis

Total Heterotrophic Bacteria (THB) Count

Ten fold serial dilution of soil prepared. Total heterotrophic bacteria count is performed on sterile nutrient agar (Oxoid) using the spread plate method (Grade, 1985). Cultures (triplicate) are incubated at room temperature, 28 $\pm$ 2^0C for 28 hours. Plates yielding counts of 30-300 colonies are chosen. The counts obtained are multiplied by the dilution factor to obtain the number of bacteria per gram of soil.

6.11.3 Total Coliform

The most frequently used indicator organism is the non-pathogen coliform bacteria *Eschericia coli*. Positive tests for *E. coli* do not prove the presence of enteropathogenic organisms but establishes faecal contamination.

For *E. coli* to be a useful organism, it must be differentiated from the non-faccal bacteria. The conventional test for the detection of faecal contamination involves a three-stage procedure (Pepper *et al.*, 1995).

1. Presumptive test

Lactose broth tubes are inoculated with undiluted or appropriately diluted water samples, and incubated at 35 ^{0}C for 24-48 hours. On incubation for 24hours, if there is no gas formation, continue for another 24 hours (Total 48hours). The tubes showing gas formation are recorded as positive and are used to calculate the most probable number of coliform bacteria in the sample. Gas formation detected in the small inverted tubes (Durham tubes) gives positive presumptive evidence of contaminations by faecal coliform.

2. Confirming Test

The presence of enteric bacteria is confirmed by streaking samples from the positive lactose broth cultures onto G. medium such as Eosin Methylene Blue (EMB) agar. Faecal coliform colonies on this medium acquire a characteristically greenish metallic sheen. Enterobacter species form reddish colonies and non lactose fermenters form colourless colonies respectively.

3. Completed Test

Select two colonies from (2) above. These are used to inoculate a tube of lactose broth with Durham tube and also a nutrient agar slant. Both the slant and tube are incubated at 35°C for 24-48 hours. The lactose broth culture is observed for gas production. If there

is evident gas production, it gives a completed test for coliforms. The observation can further be confirmed by observing a Gram stain preparation from the agar slant. Microscopic examination will reveal Gram-negative non-sporulating bacilli if coliforms are present.

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Appendix I: Past work in the GOGLME Area

TABLE 1: GULF OF GUINEA - PHYSICO-CHEMICAL CHARACTERISTICS OF SEAWATER

Physico-Chemical Characteristics	Range of water quality data from the Gulf of Guinea.		References
	Wet season	Dry season	
Ph	7.36 – 7.56	7 – 8	Ajao & Fagade (1990)
Conductivity (µS/cm)	46910.0 – 62710.0	45296.0 – 62101.0	Lekki EPZ EIA 2004.
TSS (mg/l)	<0.1 – 1.5	<1.0 – 2.0	Lekki EPZ EIA 2004.
Odour	Odourless	Odourless	Lekki EPZ EIA 2004.
DO (mg/l)	3.5 – 11.50	4.2 – 6.5	Ajao & Fagade (1990)
Temperature (°C)	25.3 - 29	27 - 32	Ajao & Fagade (1990)
Acidity			
Alkalinity			
Turbidity (FTU)	1.0 – 4.0	1.0 – 4.5	Lekki EPZ EIA 2004.
BOD_5 (mg/l)	3.49 – 4.10	3.63 – 4.15	Lekki EPZ EIA 2004.
COD (mg/l)	12.08 – 17.10	12.04 – 17.15	Lekki EPZ EIA 2004.
Salinity (‰)	0.0 - 29	11.3 – 30.2	
Colour (PtCo)	7.0 – 22.0	7.0 - 60.0	Lekki EPZ EIA 2004.
Exch. Cations ((mg/l)			
Na^+	4896.0 – 7700.0	2264.0 – 7655.0	Lekki EPZ EIA 2004.
K^+	9.80 – 6191.0	9.75 – 6209.0	Lekki EPZ EIA 2004.
Ca^{2+}	629.63 – 30959.5	620.91 – 3094.50	Lekki EPZ EIA 2004.
Mg^{2+}	423.1 – 739.20	450.30 – 5751.40	Lekki EPZ EIA 2004.
Mn^{2+}	0.20 – 6.85	0.23 – 8.95	Lekki EPZ EIA 2004.
Nutrients (mg/l)			
Nitrate	0.45 – 0.52	0.43 – 0.55	Lekki EPZ EIA 2004.
Nitrite	0.021 – 0.03	0.026 – 0.035	Lekki EPZ EIA 2004.
Phosphate	0.75 – 2.55	0.80 – 2.53	Lekki EPZ EIA 2004.
Silicate			
Heavy Metals (mg/l)			
Fe	<0.01 – 0.03	0.01 – 0.04	Lekki EPZ EIA 2004.
Cd	n.d – 0.051		Sadik. (1990)
Cu	1.59 -2.50	1.72 – 2.47	Lekki EPZ EIA 2004.
V	0.08 – 0.68	0.09 – 0.67	Lekki EPZ EIA 2004.
Zn	0.12 – 0.27	0.15 – 0.27	Lekki EPZ EIA 2004.
As			
Ba			
Cr	<0.01 – 0.02	<0.01 – 0.02	Lekki EPZ EIA 2004.
Pb	0.09 – 0.36	0.09 – 0.34	Lekki EPZ EIA 2004.
Hg	0.002 – 0.005	<0.001 – 0.005	Lekki EPZ EIA 2004.
TPH (mg/l)	<0.001	<0.001	Lekki EPZ EIA 2004.

TABLE 2: GULF OF GUINEA - PHYSICO-CHEMICAL CHARACTERISTICS OF SEAWATER

Physico-Chemical Characteristics	OML 67 and 70 (Fabino Consult, 2002)		OML 100 (Scientific Ideas, 2002)	OML 102 (ERML, 2001)	OML 67 and 70 (Triple "E", 1994)	
	Dry	Wet			Dry	Wet
Ph	7.40 - 8.60	8.20 - 9.50	8.30 - 8.90	8.80 - 8.90		
Conductivity (mS/cm)	54.21	53.49	41.5-46.0	38.8-44.9		
TSS (mg/l)				2.00-29.00		
TDS (mg/l)	38,996	3911.51		34.6-40.4		
DO (mg/l)	6.50-7.80	6.60-7.90		5.00-10.1		
Temperature (°C)	27.4-29.8	26.3-28.5				
Turbidity (FTU)	0.62	0.19				
BOD (mg/l)	1.88	0.88				
COD (mg/l)				31.2-58.0		
Salinity (%)	35.97	34.89				
Oil/Grease (mg/l)	0.21	0.19				
Exchangeable Cations ((mg/l)						
Na^+	10,995.39	10,934.23			4922.4	6798
K^+	307.69	297.92	125-133	108-134	140.6	315.5
Ca^{2+}	341.85	332	164-179	127-151	85.8	285.3
Mg^{2+}	1202.69	1107	840-924	793-1006	385.3	1126.4
Mn^{2+}	0.032	0.030			0.02	0.08
Anions (mg/l)						
NH_4^+				0.58-1.52		
NO_3^-				2.00-5.24		
Nutrients (mg/l)						
NO_3^-N	0.35	0.32			0.11	0.4
NH_4^-N	0.22	0.21			0.44	2.1
PO_4^-P	Negligible	Negligible			0.004	0.00
Heavy Metals (mg/l)						
Fe	0.265	0.256			0.18	0.37
Cd	0.045	0.0262	0.02	0.02	ND	ND
Cu	0.097	0.07	0.05	0.05	0.00	0.05
Co	0.90	0.726				
Ni	0.034	0.0176	0.10	0.10	ND	ND
V	0.061	0.0462	0.20	0.20		
Zn	0.07	0.0452	0.05	0.05	0.03	0.05
As			0.001	0.001		
Ba			0.03	0.03		
Cr	0.055	0.032	0.10	0.10		
Pb	0.047	0.025	0.20	0.20	ND	ND
Hg	ND	ND				
TPH (mg/l)			<1.00	<1.00		

TABLE 3 PHYSICO-CHEMICAL CHARACTERISTICS OF SEABED SEDIMENTS FROM PREVIOUS STUDIES CONDUCTED AROUND GULF OF GUINEA.

PARAMETER	OML 100 (2002)	OML 102 (2001)	OML 67 & 70 (2002)	
	Range	Range	Dry Season	Wet Season
pH	7.91 – 8.71	7.69 – 8.71	8.15	7.67
Conductivity (mS/cm)	12.9 – 23.2	14.7 – 37	1.995	1.936
Exchangeable Cations (ppm)				
Ca^{2+}	17,614 – 22,692	4,496 – 24,484	27.51	27.46
K	2,350 – 4,282	997 – 4,304	24.10	24.88
Mg^{2+}	6,882 – 10,343	3,725 – 9,807	22.96	23.10
Al^{3+}	26.1 – 56.8	19.0 – 66.6		
Na^{+}	----	----	41.26	42.18
Mn^{2+}	----	----	0.06	0.16
NH_4	----	----	2.16	1.81
TPH	<10.0 – 46.0	<1.0 – 69.0		
THC	----	----	66.55	59.79
Heavy Metals (ppm)				
Ba	40.0 – 129.0	21.0 – 105.0	0.011	0.063
Zn	38.0 – 92.0	20.0 – 93.0	23.50	24.64
Pb	5.00 – 14.0	3.00 – 17.0	0.09	0.03
As	1.43 – 5.28	<1.00 – 3.20	----	----
Ni	11.0 – 31.0	8.00 – 35.0	0.12	0.14
Cr	18.0 – 38.0	10.0 – 73.0	0.37	0.12
Cu	6.00 – 14.0	3.00 – 16.0	0.49	0.52
V	<0.20 – 31.0	<0.20 – 56.0	0.07	0.07
Cd	<0.02	----	----	----
Fe	----	----	728.07	737.78
Particle Size (%)	Clayey 28.0 – 52.7Clay 25.4 – 62.1 Silt	Silty Clay 8.30 – 11.2 Clay 38.7 – 56.9 Silt	89.98% clay 9.97% Silt 0.42%	89.28% Clay 10.66% silt 0.62%
Anions (ppm)				
NO_3^-	----	----	----	----
NO_2^-	----	----	0.76	0.51
PO_4	----	----	3.19	2.58
SO_4	----	----	23.30	20.41
Cl^-	----	----	59.30	60.12

TABLE 4: HEAVY METAL, TOTAL ORGANIC CARBON, AND TOTAL HYDROCARBON LEVELS OF SEABED SEDIMENTS FROM PREVIOUS STUDIES CONDUCTED AROUND GULF OF GUINEA.

PARAMETER	Range		References
Heavy Metals (mg/kg) Dry Wgt.			
Zn	22.13 – 193.55		Ajao & Fagade (1990)
Pb	76.93 – 275.27		Ajao & Fagade (1990)
Mn	310.36 – 847.66		Ajao & Fagade (1990)
Ni	37.71 – 203.09		Ajao & Fagade (1990)
Cr	n.d – 169.40		Ajao & Fagade (1990)
Cu	n.d – 36.70		Ajao & Fagade (1990)
Co	n.d – 462.44		Ajao & Fagade (1990)
Cd	3.30 – 9.50		Ajao & Fagade (1990)
Fe	5876 – 14068.2		Ajao & Fagade (1990)
THC (µg/g)	4.12 – 109.33		Ajao & Fagade (1990)
TOC (% By Wgt.)	Wet 3.75 - 31.20	Dry 0.48 – 3.85	Ajao & Fagade (1990)

TABLE 5: HEAVY METAL LEVELS IN FISH TISSUES FROM PREVIOUS STUDIES CONDUCTED AROUND GULF OF GUINEA.

PARAMETER	Sadik, (1990)	Unyimadu, et al.(2004)
Heavy metals.	Range (mg/Kg)	Range (µg/g)
Zn	2.8 – 18.6	1.66 – 3.83
Pb	n.d – 0.05	n.d – 2.67
As		
Ni	n.d – 0.06	
Cr		n.d
Hg	n.d – 0.63	
V		
Cd	n.d – 0.19	n.d – 0.21
Mn		0.44 – 0.98

Appendix 2. Settling times for Pipette Analysis according to Wadell's modification of Stokes's Law (After Friedman and Johnson, 1982)

Ø	Diameter (mm)	Description	Depth (cm)	Time of Settling		
				hr	min	sec
4	0.0625	Silt	20	00	01	00
5	0.0313	Very coarse Silt	10	00	02	59
6	0.0156	Coarse silt	10	00	11	59
7	7.8125×10^{-3}	Medium silt	10	00	49	51
8	3.906×10^{-3}	Fine silt	10	03	12	00
9	1.95×10^{-3}	Very fine silt	7	08	58	00
10	9.766×10^{-4}	Clay	5	25	43	00

GRAIN SIZE ANALYSIS DATA SHEET

SIEVE SIZES			SAMPLE:				SAMPLE:				SAMPLE:			
Mm	Un	ö	Freq	Cum. Freq.	Cum Freq %	Indiv. Pct.	Freq	Cum. Freq.	Cum. Freq. %	Indiv. Pct	Freq	Cum. Freq.	Cum. Freq. %	di Pe
Pan														
TOTAL														

AN M_z = $\frac{ö16 + ö50 + ö84}{3}$

GRAPHIC STD.DEV. Ö I

$\frac{ö16}{} + \frac{ö95 - ö5}{6.6}$

GRAPHIC SKEWNESS SK_I

$\frac{+ ö84 - 2ö5}{84-ö16)} + \frac{ö5 + ö95 - 2ö50}{2(ö95 - ö5)}$

TOSIS – K_G $\frac{ö95-ö5}{2.44(ö75-ö25)}$

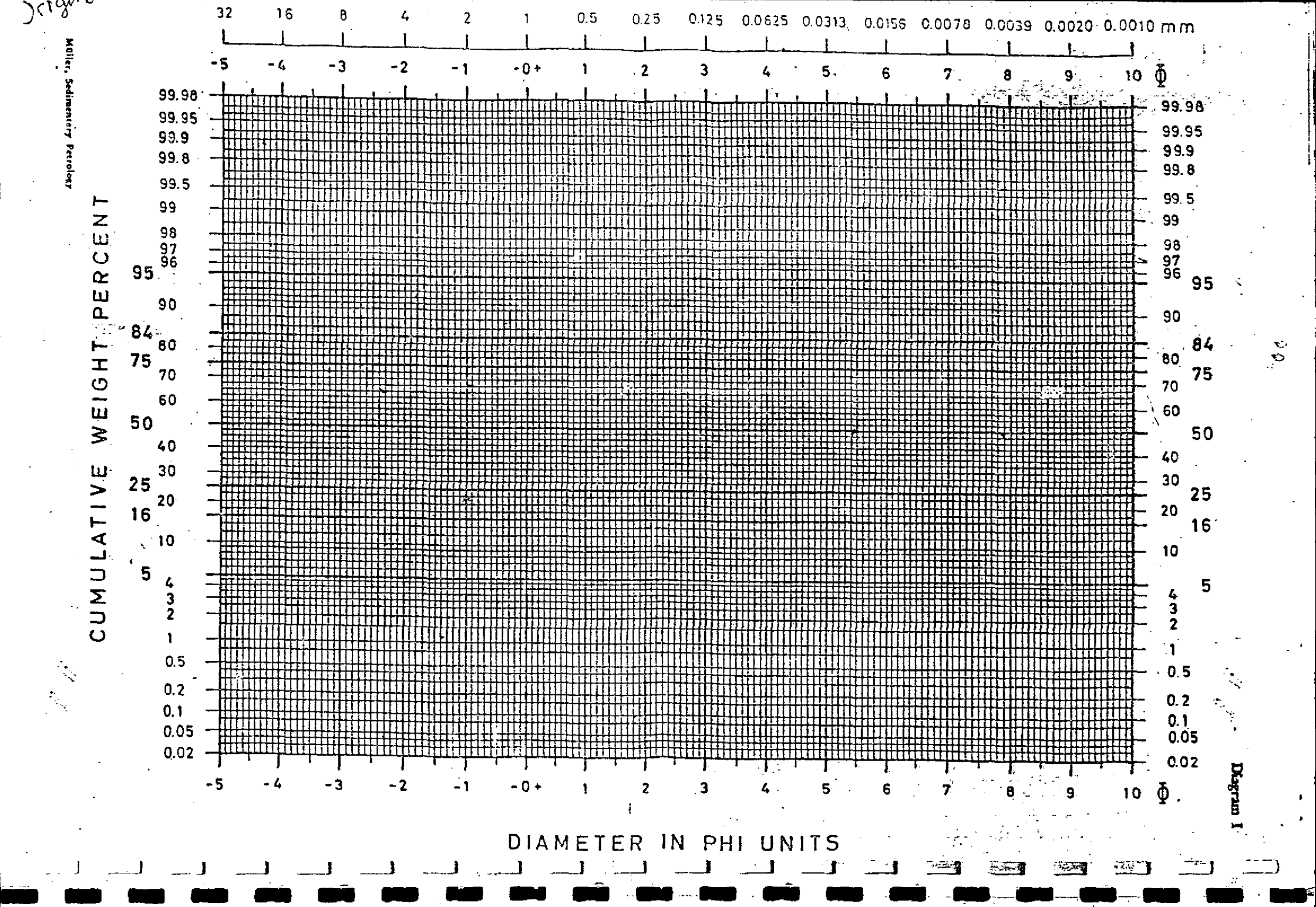
ANALYST.....

DATE.....

GRAIN SIZE ANALYSIS DATA SHEET

SIEVE SIZES			SAMPLE:				SAMPLE:				SAMPLE:			
Mm	Um	ϕ	Freq	Cum. Freq.	Cum Freq %	Indiv. Pct.	Freq.	Cum. Freq.	Cum. Freq. %	Indiv. Pct.	Freq.	Cum. Freq.	Cum. Freq. %	Indiv. Pct?
Pan														
TOTAL														
MEAN M_z $\frac{\phi 16 + \phi 50 + \phi 84}{3}$														
INC. GRAPHIC STD.DEV. σ_I $\frac{\phi 84 - \phi 16}{4} + \frac{\phi 95 - \phi 5}{6.6}$														
INC. GRAPHIC SKEWNESS SK_I $\frac{\phi 16 + \phi 84 - 2\phi 5}{2(\phi 84 - \phi 16)} + \frac{\phi 5 + \phi 95 - 2\phi 50}{2(\phi 95 - \phi 5)}$														
KURTOSIS – K_G $\frac{\phi 95 - \phi 5}{2.44(\phi 75 - \phi 25)}$														

ANALYST..... DATE .....


32 16 8 4 2 1 0.5 0.25 0.125 0.0625 0.0313 0.0156 0.0078 0.0039 0.0020 0.0010 mm
-5 -4 -3 -2 -1 -0+ 1 2 3 4 5 6 7 8 9 10 Φ
99.98 99.95 99.9 99.8 99.5 99 98 97 96 95 90 84 80 75 70 60 50 40 30 25 20 16 10 5 4 3 2 1 0.5 0.2 0.1 0.05 0.02
CUMULATIVE WEIGHT PERCENT
DIAMETER IN PHI UNITS
Müller, Sedimentary Petrology
Diagram 1