STANDARD PROTOCOL FOR CONDUCTING PRE-OPERATIONAL ENVIRONMENTAL SURVEILLANCE AROUND NUCLEAR FACILITIES

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| 60 | *Abstract :* This document presents the standard procedures for evaluation of site specific environmental transfer factors around NPP sites. The scope of this document is to provide standard protocol to be followed for conducting pre-operational environmental surveillance around nuclear facilities. Such surveillances have been proposed to be carried out by university professionals under DAE-BRNS projects. This document contains a common methodology in terms of sampling, processing, measurements and analysis of elemental/radionuclides, while keeping the site specific requirements also in place. |

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SUMMARY

This document presents the standard procedures for evaluation of site specific environmental transfer factors around NPP sites. The scope of this document is to provide standard protocol to be followed for conducting pre-operational environmental surveillance around nuclear facilities. Such surveillances have been proposed to be carried out by university professionals under DAE-BRNS projects. This document contains a common methodology in terms of sampling, processing, measurements and analysis of elemental/ radionuclides, while keeping the site specific requirements also in place.

PROTOCOL FOR CONDUCTING PRE-OPERATIONAL ENVIRONMENTAL SURVEILLANCE AROUND NUCLEAR FACILITIES

SCOPE OF THE DOCUMENT

The scope of this document is to provide standard procedures (Protocol) to be followed for carrying out pre-operational environmental surveillance around nuclear facility. The pre-operational environmental surveillance around a nuclear power plant is essential to assess the impact of plant operations on the environment. In Indian scenario such surveillance is mandatory to fulfill the regulatory requirements before the commissioning of the plant. This document is prepared to provide a common methodology in terms of sampling, processing and measuring of radiological and conventional parameters in various environmental matrices while keeping the site specific requirements also in place.

1.1 INTRODUCTION

The operations of nuclear facilities results in low level radioactive effluents, which are required to be released into the environment. Though the effluents from nuclear installations are treated adequately and then released in a controlled manner under strict compliance of discharge criteria, the effluents undergo dilution and dispersion. However, there is possibility of concentration by the biological process in the environment.The simplified pathways by which the released radionuclides reach man are shown below :
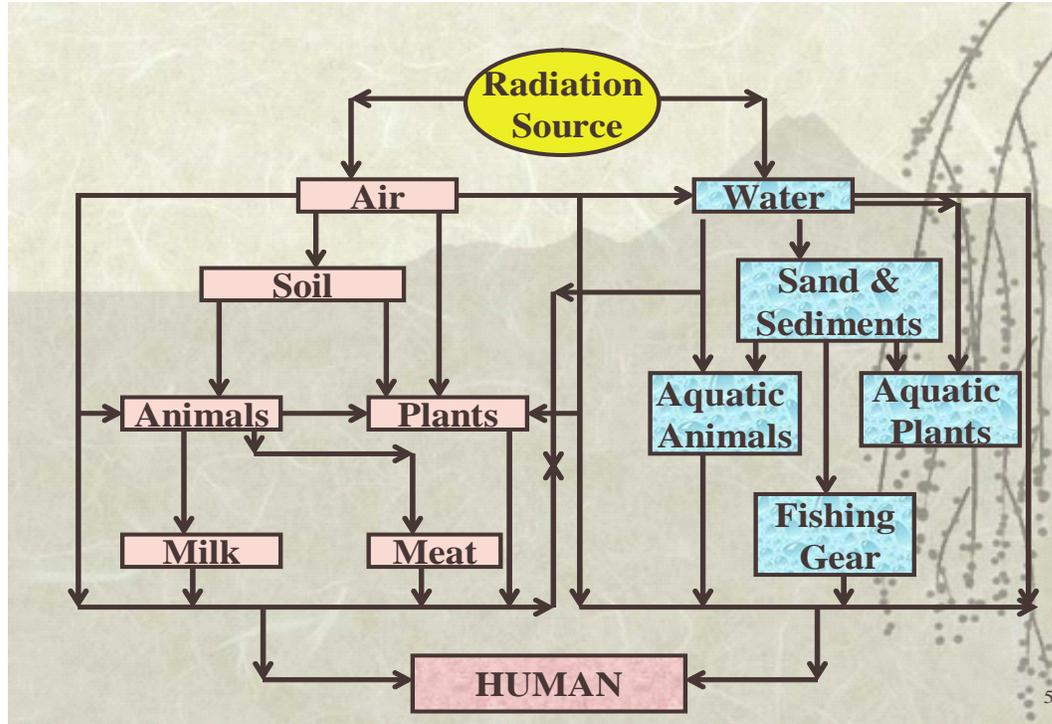
Thus it is imperative to conduct radiological environmental surveillance around the proposed nuclear facility. The pre-operational monitoring helps in assessing the impact of operations of facility during its operational phase and also serves as the basis for estimation of radiation doses to public due to releases from plant

The basic objective of environmental surveillance around the nuclear facility such as nuclear power plant is to evaluate and control the radiation exposure received by the members of the public during the course of plant operation. A systematic planned study is essential to establish the baseline data on natural and fallout radioactivity in various environment matrices before the plants go into operations. The environmental surveillance around the facility also includes the measurements on conventional parameters in respect of air and water quality in the surroundings of nuclear facility. The collections of local meteorological parameters during pre-operational studies are important to establish wind pattern in the surroundings of proposed facility.

In order to fulfill the objective of pre-operational surveillance comprehensive monitoring and measurements of radiological, conventional and meteorological parmeters in the surroundings of proposed facility is needed to be planed. The plan requires periodic collection and analyses of various environmental matrices from atmosphere, terrestrial and aquatic realms. This also includes dietary items such as water, cereals, pulses, meat, fish, milk, egg etc. for their radioactivity contents. Environmental samples are collected on regular basis from various locations surrounding the nuclear facility upto a distance of 30 km from the proposed plant site. The sampling locations are selected on the basis of wind pattern, utilization of environment and population clusters around the facility. The type of samples are selected on the basis of potential pathways to man. The pre-operational surveillance programme should be conducted before two to three years of commissioning the proposed nuclear facility. This covers the seasonal cycles and to draw effective conclusions on baseline radiological data, air quality, water quality around proposed facility can be established.

1.2 PRE-OPERATIONAL MONITORING

Pre Operational monitoring serves as the basis for estimation of radiation doses to public due to releases from the operating facility. The following activities are associated with pre-operational surveillance around nuclear facility.

1. Preparation of local map upto a distance of 30 km around proposed project site.
2. Collection of information on environment utilisation by the public with the help of local revenue and statistical departments.
3. Collection of data on geological and hydrological features of local environment from the available literature and nearby academic institutes.
4. Collection of data on demography and dietary habits of public.
5. Collection of local meteorological parameters such as wind direction, wind speed, solar radiation, rain fall, ambient temperature , relative humidity, etc. over two years and statistical analyses of collected data to establish wind pattern around site
6. Identification of sampling locations using GPS and types of samples to be collected from the identified locations.
7. Collection of data on direct radiation exposure in and population centers upto a distance of 30 km from site.

8. Collection and analysis of various environmental samples for establishing the base line data on natural and fallout radioactivity in the environment
9. Collection of water samples from the nearby water bodies, public well etc. to establish their water quality parameters.
10. Collection of air samples in the surroundings of proposed site and analyse various air quality parameters

The information on first three activities may be obtained by mutual interactions with the authorities at local and district levels. The data on demography and food habits of public may be obtained as given in the standard protocol for demographic and epidemiological survey around nuclear facilities (BARC/2007/E/018, 2007). However, for establishing the baseline data on radiological parameters, water quality parameters and air quality parameters in the surroundings of proposed nuclear facility, rest of the listed activities are required to be studied for at least two –three years prior to the commissioning the facility.

This document is prepared to provide a common methodology in terms of sampling, processing and measuring of radiological and conventional air & water quality parameters in various environmental matrices while keeping the site specific requirements also in place. These aspects are covered in details in the following sections.

1.3. DIRECT RADIATION EXPOSURE

Extensive gamma radiation survey needs to be carried out in and around villages located in the surroundings of site up to a distance of 30 km. The radiation survey data are useful to establish the ambient radiation levels in environment of nuclear site.

1.3.1 PROCEDURE

The gamma radiation levels are monitored using a sensitive survey meter which can read the radiation in nSv/h levels. The calibrated BICRON ANALYST type of survey meter are adequate for the purpose.

1.4. COLLECTION OF SAMPLES AND ANALYSIS FOR NATURAL AND FALL OUT RADIOACTIVITY

Different types of environmental samples from the atmospheric, terrestrial and aquatic environs of the proposed site are required to be collected and analysed the levels of various radionuclides of natural (U-238, Th-232 and K-40) and fallout (Sr-90 and Cs-137) origin. These samples are processed and analysed by gamma spectrometry and radiochemical separation as per the prescribed standard procedures given in the Section -1 this document.

1.5. WATER QUALITY PARAMETERS

The physicochemical parameters in water samples are essential to establish the water quality during pre-operational phase. The water samples are also required to analyse for essential, toxic and selected trace elements. This helps to the water quality of the surroundings and also to compare with the analyses during operational phase. The details of water quality parameters and their procedure are given in Section -2 of this document.

1.6. AIR QUALITY PARAMETERS

The ambient air quality needs to be assessed by estimation of common air quality parameters. The Section-3 gives the details procedures for the determination of SO_2, NO_2
And air particulate in air samples.

1.7. METEOROLOGICAL PARAMETERS

The local meteorological parameters are essential to know the atmospheric dispersion of the gaseous release from the facility. The Section-4 describes various meteorological parameters, their collection and uses for evaluating the local diffusion climatology and surface observations. Appropriate formats for presentation of

2. SAMPLING

2.1 SAMPLING PROGRAMME

 The collection of valid samples is the vital first step. Sampling should be done with the same care as the analysis, and both should be done with a rigor that is appropriate for the project at hand.

A variety of samples may be required for the purpose of obtaining concentrations in different matrices which will lead to serve the objective. Sampling must be carried out based on certain specific criteria so that representative sample can be collected. Usually, the crucial decisions in planning a sampling program are Sampling locations, Sampling frequency, Sample matrices of relevance etc.

The sampling locations need to be identified based on the wind pattern, environmental usage and utilization of the environment. It should include locations up to a distance of 30 km from the site. In general the sampling near source may be more frequent as compared to far distances. The samples should be collected as available in a particular season and the number of samples should be at least five for each species (eg. 5 spinach samples within 30 km radius and the corresponding soil samples). The collected samples must be identified and logged in the record book according to their date and locations.

Sampling locations, matrices and frequencies are selected on the basis of:
a. Distance from the source
b. Predominant wind affected sector
c. Downstream water flow from discharge point
d. Discharge point use/consumption of matrix and its contribution and importance in internal exposure.
e. Production centre and availability of matrix
f. Population using the matrix
g. Coverage of all sectors with appropriate frequency
h. Frequency and number reduces with distance
i. Radionuclide released and recipient media and its exposure pathways.

2.2 TYPE OF SAMPLE

Samples to be collected for evaluation of transfer factors can be mainly categorised as of terrestrial samples and aquatic (samples of marine or fresh water origin).

2.2.1 SAMPLES FROM TERRESTRIAL ENVIRONMENT

Soil, grass, vegetation, food crops, fruits, milk, vegetables, meat etc. Ground water samples from wells and bore wells constitute the main source for studying terrestrial subsoil movement of radioactivity.

2.2.1.1 SOIL

Soil sampling is carried out with intention to mainly evaluate root uptake leading to environmental transfers. Soil sample should be collected from an undisturbed area. For study of transfer factors, area has to be nearly covering the root spread. Samples from different spots covering a depth of 15 to 20 cm upto which the ingrowth of nourishing roots is expected, has to be covered. A small pickaxe or a hand-scoop can be used for sampling.

2.2.1.2 GRASS

Grass or other types of animal forage are sampled from known area. A 1m x 1m area wooden frame is to be laid over the area and the grass within the frame is to be cut above 4 cm height from ground to minimize soil adherence and to represent the portion normally used as fodder. If the grass is grown only to a small height, or if the end objective is to study transfer factors, the grass must be cut just above the ground. Grass from 3 to 4 locations in an area may be composited to get a representative sample.

The green grass can be collected and stored in perforated plastic bags. Fresh weight is to be taken on reaching the laboratory.

2.2.1.3 VEGETABLES/VEGETATION

For evaluation of contribution of a pollutant to environment from a source, vegetables and vegetation have to be collected from the fields located in the environment. A composite sample, about 4 kg in weight is to be collected from the locality, from

different plants distributed at the locality. 2 kg is normally sufficient for analyses, the rest being for storage. Samples can be collected in perforated polythene bags and stored under refrigeration. Fresh weight is to be taken at the earliest.

Vegetables and vegetation vary from place to place and the sample chosen should be representative for the location.

2.2.1.4. FOOD CROPS

Rice, wheat, millets and pulses are the main food crops in the country. For study of transfer factors the samples have to be collected from the field along with soil sample. For dose evaluation, they can be collected from the field or from granaries known to store crop from the locality. About 2 kg of sample should be adequate for radiochemical estimation and storage.

2.2.1.5 MILK

Milk should be collected from dairy farms where milk is processed for distribution or pooled from 5 milk producers and pooled to make a representative sample. 2 liters milk is needed to be sampled, 1 liter for immediate analysis and 1 liter as standby. 5 ml of 5% formalin is added per liter if milk is to be preserved for long periods. For short duration, refrigeration is enough.

2.2.1.6 MEAT

Fresh meat of cattle or sheep is to be collected from local abattoir or local market in case there is no abattoir. The sample of 2 kg soft tissue (about 4 kg total) is to be analyzed. The sample can be brought in plastic bags and stored in a refrigerator or deep-freeze.

2.2.1.7 GROUND WATER

Main ground waters to be studied in terrestrial environment are well waters and bore well waters. For study of contribution to dose about 20 liter of water needs to be analyzed since the levels are likely to be very low. In case of monitoring bore wells and open wells near a waste storage facility, a volume of 1 liter is adequate for studying ground water movement or seepage of the pollutant.

2.2.2 AQUATIC MONITORING

Fresh water, sea water, aquatic organisms like fish (fresh water and marine) shore sediment, bottom sediment and bottom cores, aquatic biota and aquatic plants cover the spectrum of samples of aquatic origin.

2.2.2.1 WATER SAMPLES: 10 - 20 liter of water from water body at desired locations should be collected in plastic containers. At locations where treated effluents are discharged into the aquatic system, it is desirable to have a continuous sampler which pumps small quantity of water from the location to a container. This will give the time averaged concentration.

2.2.2.2 SEDIMENT: Shore sediment is collected from top soil, using procedure same as surface soil, lake bed, river bed and sea bed are sampled using grab samplers (Ekman Dredge). From each location, two or three grabs should be collected and pooled. 1 to 2 kg samples are collected and prepare a composite sample to represent the sample of that location.

2.2.2.3 AQUATIC BIOTA / PLANTS: The phytoplankton and zooplankton samples from the water body may be collected by passing a known volume of water through plankton net of bolting silk. The samples should be preserved in 4% formalin. The aquatic plants have to be collected, dislodging silt with thorough washing. Samples should be collected in plastic bags with perforations and preserved in deep freezer.

2.2.2.4 FISH AND AQUATIC ORGANISMS: Fish samples are collected from fish landing centres or brought directly from the boats or trawlers. These samples have to be collected depending on the availability, with the help of local fishermen. It would be better if variety of samples can be collected so that study on preference uptake of a particular radionuclide may be carried out. About 1 kg of fish is normally sufficient for a single analysis. Marine organisms like Oysters, Crabs, Clams, Sponges concentrate radionuclides and are good indicators for specific radionuclides should also be collected. Samples collected in plastic bags should be transferred to ice-box and subsequently preserved in deep freeze prior to analysis.

2.3 SAMPLE PRESERVATION, PROCESSING AND PRECONCENTRATION

Environmental samples are collected at site and generally require preservation prior to being taken up for analysis. Initial process like washing, drying and preliminary preparation is needed for carrying out instrumental, radiometric or elemental analyses.

Take up the sample immediately for gamma counting taking into consideration of short lived radionuclides.

A) SOIL

1. Separate rocks and pebbles
2. Dry at $110\ ^0C$, weigh.
3. Powder
4. Sieve through 70 mesh
5. Weigh known quantity into standard container.
6. Subject to gamma spectrometry with HPGe detector.
7. Take up 10-100 g for radiochemical separation

B) GRASS AND VEGETATION & VEGETABLES:

1. Weigh the sample
2. Wash the samples
3. Remove non-edible portions preserve in refrigerator till its processing.
4. Weigh again (weight of edible portion)
5. Dry at $110\ ^0C$
6. Weigh again (Dry weight)
7. Pack in standard container
8. Count in HPGe or NaI(Tl) detector gamma spectrometer with MCA.
9. Transfer to tared Silica dish. Ash at $450\ ^0C$ in a muffle furnace. Weigh (Ash weight)
10. Take up for radiochemical analysis.

C) FOOD CROPS

1. Transfer 1 kg (dry rice/wheat, millet, cereal) into a standard container.
2. Count in a NaI(Tl) detector based or HPGe detector based gamma spectrometry.

3. Transfer to tared Silica dish. Ash at 450 ^{0}C in muffle furnace weigh (ash weight)

4. Take up ash for radiochemical analysis.

D) MILK

1. Measure 1l milk into a large tared stainless steel container.

2. Evaporate to dryness

3. Dry ash at 450 ^{0}C.

4. Weigh again (Ash weight)

5. Transfer to a standard container

6. Count for gamma activity (measure the height of the sample)

7. Take up for radiochemical analysis

E) MEAT

1. Wash and preserve in refrigerator till it is processed.

2. Remove non-edible portion (weigh - fresh weight)

3. Dry at 110 ^{0}C (weigh - dry weight)

4. Ash at 450 ^{0}C (weigh - ash weight)

5. Transfer ash to a standard container and subject to gamma spectrometry.

6. Take up ash for radiochemical analysis

F) FISH AND AQUATIC ORGANISMS

1. Separate and classify the organisms. Weigh each group (total weight)

2. Wash the sample and preserve in refrigerator till it is processed

3. Separate edible portion, about 1 kg (fresh weight)

4. Dry at 110 ^{0}C and powder

5. Transfer dry powder to a standard container and subject to gamma spectrometry

6. Ash at 450 ^{0}C in a tared silica dish and weigh the ash

7. Take up ash for radiochemical separation.

G) AQUATIC BIOTA / PLANTS

1. Dislodge deposited silt by thorough washing and preserve in 4% formalin.

2. Drain dry, weigh (fresh/wet weight). About 1 kg required.

3. Dry at 110 ^{0}C, powder and weigh

4. Transfer to tared standard container and subject to gamma spectrometry in HPGe detector.

5. Transfer dry powder to tared silica dish. Ash at 450 ^{0}C. Weigh

6. Take up ash for radiochemical separation.

H) BOTTOM SEDIMENT

1. Pass (or push if necessary) using a rubber stopper through 10 mesh to remove stones and sand.

2. Dry at 110 ^{0}CZ, take dry weight.

3. Ash at 450 ^{0}C - ash weight.

4. Powder

5. Transfer weighed quantity into standard container, count for gamma emitters

6. Take up 10-100 g for radiochemical separation.

I) SHORE SEDIMENT

1. Remove stones and pebbles

2. Weigh (wet weight)

3. Dry at 110 ^{0}C, weigh (dry weight)

4. Powder, Sieve through 70 mesh.

5. Weigh, transfer to standard container and analyse for gamma emitters in HPGe detector.

6. Take up 10-100 g for radiochemical separation.

J) FRESH WATER SAMPLES

1. Filter a known volume of water using Whatman 42 filter paper. Acidify the sample with Conc. HNO_3 (3ml/l).

2. Evaporate to dryness for carrying out elemental analysis. Or use appropriate pre--concentration of sample for radiometric analysis.

3. Take up for radiochemical analysis

K) SEA WATER SAMPLES

1. Filter a known volume of water using Whatman 42 filter paper. Acidify the sample with Conc. HNO_3 (3ml/l).

2. The sample is then pre-concentrated for carrying out radiometry or instrumental analysis such as gamma spectrometry.

3. Take up for radiochemical analysis

A good quality map of study area needed to be prepared showing all the sampling locations and type of samples collected from these locations.

The map should also show the boundary circles of 5, 10, 15, 20 and 30 km radius around the study site. Each radial zone should be divided into 16 directional sectors as shown in FIG. 1 of the typical map of Kudankulam site.

FIG.1   KUDANKULAM SITE AND ITS ENVIRONMENT

3.0 SAMPLE PREPARATION AND RADIOCHEMICAL ANALYSIS

3.1 INTRODUCTION

The sample preparation for activity estimation depends upon the type of sample and radionuclides to be analysed and the activity levels. Gamma emitters are estimated in fresh, dried or ashed samples after filling in a container of suitable geometry by direct gamma spectrometry depending upon activity levels. Volatile radionuclides such as radioiodine are estimated in fresh samples or with special precautions to avoid loss by volatalisation. Beta and alpha emitters are estimated after radiochemical separation. For the purpose of radiochemical separation, it is necessary to first solubilise the sample to mobilise all detectable radionuclides from the sample matrix. Generally the following methods or a combination of them are adopted depending upon the sample matrix and objective of the analysis.

3.2 INITIAL TREATMENT

3.2.1 ACID LEACHING METHOD

It has been observed that strong nitric and hydrochloric acid leaching suffices to mobilise most of the radionuclides from environmental samples (e.g. marine and fresh water sediment, ash of tissue, vegetation, crop, milk etc.)

3.2.2 ALKALI FUSION AND HYDROFLUORIC ACID TREATMENT

Alkaline fusion with $NaOH$-$NaNO_3$-Na_2CO_3 mixture enables solubilisation of silicates and mobilising the radionuclides (e.g. grass, glass fiber air filter paper, ash of biological samples). In cases where the entire sample must be brought into solution (e.g. soil/sediment), initial acid digestion followed by a series of hydrofluoric acid treatment to volatalise silica and finally sodium carbonate fusion of the acid residue is carried out. When volatile radionuclides such as radioiodine is to be analysed, alkaline fusion of fresh samples is always resorted to (e.g. thyroid glands, other tissue samples, algae etc.). In general the analyst dealing with a complex system will be well advised to adopt the least complex and least drastic treatment which will achieve his objectives.

3.3 GENERAL PROCEDURE FOR RADIOCHEMICAL ANALYSIS

3.3.1 INTRODUCTION

In general, radionuclides are present in biological samples at the level of a few atoms per gram and it is necessary to add inactive carriers, hold back carriers and tracers to ensure quantitative recovery and estimate the recovery of the radionuclide. Some of the commonly encountered radioelements and the carriers and tracers to be used are tabulated below.

Radioelement	Carrier/Tracer to be added
Radioiodine	10 mg/ml I as KI
Radiocesium	20 mg/ml Cs
Radiostrontium	20 mg/ml Sr, 5 - 20 mg/ml Ba,
	10 mg/ml Y, 5 mg/ml Fe, 100 mg/ml Ca
Radiocobalt	10 mg/ml Co
Radionickel	10 mg/ml Ni
Radiocerium	10 mg/ml Ce
Plutonium	2 dpm/ml Pu-242 or Pu-236
Americium	2 dpm/ml Am-243
Polonium	2 dpm/ml Po-209

1. Prepare the carrier solutions from AR grade nitrate or chloride salts in 1M HNO_3 or HCl. Standardize and store in appropriate containers.

2. Store the tracer solution in 3M acid solution.

If sequential analysis for multiple radionuclides is adopted, add all the necessary carriers and tracers at the initial stage and allow equilibrating with the sample.

3.3.2 BIOLOGICAL SAMPLES

1. Keep aliquot for volatile radionuclides (e.g. Isotopes of I, Ru, Po) separately if necessary

2. Transfer tared sample to a porcelain dish or an enamel tray and dry at 110°C in an air oven.

3. Transfer the dried sample to a silica dish and char on low flame till fuming stops

4. Place the charred sample in the silica dish in a muffle furnace for ashing at 450°C for 16 hours or till white ash is obtained. Higher temperature will result in the loss of Cesium.

5. Weigh the ash for determination of ash content.

6. Take 3-20g ash for analysis, depending on the expected activity levels decided by the samples and sampling locations.

7. Proceed to step 8 for acid leaching or step 16 for alkali fusion.

8. **Acid leaching method (steps 8 to 12)**

   Add the carriers/tracers for respective determination and measured volume (30-60 ml) of Conc. HNO_3 to the ash sample and evaporate to dryness.

9. Repeat step 8 twice and dry till brown fumes are removed. If the residue is still brown, add 10 ml HNO_3 and a few drops of $HClO_4$, cover with a watch glass, heat to boil and finally remove white fumes by low heating on hot plate.

10. Add measured volume (5 to 20 ml) of Conc. HCl and evaporate to dryness. (About 1ml per gram of ash is required to remove HNO_3 fumes completely.

11. Extract the residue with 30 ml of hot 1:1 HCl thrice, centrifuge and collect the supernatant solution.

12. Add 30 ml of 0.1 N HCl to the residue stir well and centrifuge. Collect the supernatant and mix with the solution in step 11. Discard residue if any.

13. Add 6 N NaOH to the solution till it becomes alkaline and then 10 ml of saturated sodium carbonate solution and centrifuge. Preserve the supernatant for Cs.

14. Dissolve the precipitate with 1:1 HNO_3 and proceed for determination of radionuclides of alkaline earth metals, transition metals, rare earths, actinides, lead, phosphate etc.

15. Acidify the supernatant solution from step13 with 1:1 HNO_3 and proceed for cesium estimation.

16. **Alkali Fusion Method (steps 16 - 23) :**

   For samples containing excessive silica such as grass or vegetables etc… alkali fusion method is adopted. Take 3-20 g of ash in a nickel/s.steel crucible and add the necessary carriers/tracers. Dry under infra-red lamp.

17. Add three time by weight of fusion mixture (NaOH, NaNO$_3$, Na$_2$CO$_3$, (5:2:1) and heat over a low flame to a clear melt.
18. Continue strong heating for 10 minutes.
19. Allow the fused material to cool completely. Soak the mass in distilled water and heat.
20. Transfer the fused mass and water to a beaker with distilled water washings and heat till the lumps disintegrate completely.
21. Filter the solution through Whatman 41 filter paper. Wash the residue with distilled water.
22. Acidify the filtrate from step 21 with 1:1 HNO$_3$ and proceed for radiocesium estimation.
23. Dissolve the precipitate from step 21 with 1:1 HNO$_3$ and proceed for analysis of radiouclides of barium, strontium, cobalt, nickel, cerium, plutonium, americium etc. Discard the residue if any.

Note: When acid leaching method is adopted for the separation of Sr, matrices containing excessive sulphate ions will require special attention to avoid loss of Sr as insoluble residue. Generally, addition of 20 mg of Ba carrier will prevent such losses. Alternatively, (if only 5mg Ba carrier is added) the insoluble residue after acid leaching (step 12) is digested with saturated Na$_2$CO$_3$ solution to convert the insoluble sulphate to carbonate and centrifuged. The supernatant is discarded and the residue dissolved in 1:1 HCl and mixed with the original acid extract (step 11).

3.4 ESTIMATION OF TRITIUM IN ENVIRONMENTAL SAMPLES

3.4.1   ESTIMATION OF TRITIUM IN WATER

To determine tritium in water, distill the water sample to remove interference from non-volatile quenching and radioactive materials. Prepare standard tritium and blank samples and count simultaneously to overcome errors due to ageing of the scintillation medium or instrumental drift.

LSA: Packard 1550 Tricarb / Packard TRSL 3170
Background: 6 cpm

Scintillation Cocktail: 15 ml Dioxane based scintillator

Sample volume: 4 ml

Counting time: 6000 s

For special investigations, however, it is necessary to use special low background counters and counting parameters are as follows.

LSA:

Background: 0.7 - 0.8 cpm

Scintillation cocktail: 10 ml Instagel

Sample volume: 10 ml

Counting time: 20000 s

Distillation Apparatus: Standard distillation flask, heating mantle and condenser assembly with a trap.

3.4.1.1 REAGENTS

Scintillation cocktail - I (Dioxane based scintillator)

1. 1, 4-dioxane   :   1 l
2. Naphthalene   :   100 g
3. 2, 5-diphenyloxazole (PPO) : 7 g
4. 1, 4-di[2-(phenyloxazolyl)]benzene (POPOP) : 120 mg

Scintillator Solution: Mix the above reagents thoroughly in a clean dry beaker, stir, filter and store in an amber coloured bottle, in the dark.

Scintillation cocktail – II Instagel

3.4.1.2 PREPARATION OF WATER SAMPLES

1. Take 15ml of sample, add 1 pellet of NaOH, a few grams of $KMnO_4$ and distill slowly. The distillation flask should be provided with a trap to prevent NaOH from spraying over the condenser. Collect the distillate in a clean dry flask.

2. If water sample is coloured, add about 2 g of activated charcoal, stir well, allow settle and filter. Collect the filtrate and distill as in step 1.

3.4.1.3 PROCEDURE

1. Pipette 15 ml of scintillator solution - I and 4 ml of sample into a low background counting vial (20 ml capacity).

2. Prepare a blank sample, in the same manner as the sample, i.e. consisting of 4 ml of blank water and 16 ml of scintillator solution. The water for blank should be obtained from areas where there is minimum tritium intrusion and stored in air tight containers at all times.

3. Prepare a standard in the same manner as the sample, i.e. consisting of 16 ml scintillator solution and 4 ml of tritiated water containing a known amount of tritium activity.

4. Keep the vials in sample changer of LSA, wait and cool the samples to the temperature at which the liquid scintillation spectrometer is operated.

5. Count the samples, standard and blank vials in the LSA equipment at least twice each.

3.4.1.4 CALCULATION

Liquid Scintillation Analysers are generally provided with automatic calculation of activity, taking care of background subtraction, averaging, quench correction and efficiency.

However, steps are given below for manual calculation of efficiency and activity in air.

Calculate the counting efficiency from the formula:

$$E = \frac{[C_{st}/t_1 - C_2/t_2]}{A_{st}}$$

Where E = counting efficiency

C_{st} = gross counts of standard, in t_1 seconds.

C_2 = background counts in t_2 seconds.

A_{St} = tritium activity of standard, in disintegrations per second

The tritium content of water sample is given by the formula:

$$A = \frac{[C_1/t_1 - C_2/t_2] \pm 2SD}{E \times V}$$

Where A = tritium content, in Bq/ml

C_1 = gross counts of (sample + background) in time t_1 seconds

C_2 = background counts in time t_2 seconds

SD = the standard deviation $\pm [C_1/t_1{}^2 + C_2/t_2{}^2]^{\frac{1}{2}}$

V = volume of the sample taken for counting (ml).

3.4.2 ESTIMATION OF TRITIUM IN BIOLOGICAL SAMPLES

Tritium may be present as tissue free and tissue bound form in biological samples like dietary items.

3.4.2.1 ESTIMATION OF TISSUE FREE WATER TRITIUM (TFWT)
a.   EXTRACTION OF AQUEOUS TRITIUM FRACTION

The analytical procedure for H-3 extraction in biological matrices involves freeze-drying of the biological samples such as vegetation, fish etc. under vacuum. Each sample is extracted separately and the tissue free water of the biological sample is collected in a special trap. Fig. 3.1 is a simple system used for the purpose.

b. PROCEDURE FOR VEGETATION, VEGETABLE, FISH, WEEDS ETC.

1. Cut the sample (about 50-100 g) into small pieces of 0.5 to 1.0 cm size with scissors and transfer to a distillation flask.
2. Connect the flask to the freeze drying equipment as shown in Fig. 3.1
3. Fill the container with liquid nitrogen and wait for about ten minutes to cool.
4. Start the vacuum pump by opening the valve slowly.
5. Keep refilling the container with liquid nitrogen whenever the liquid nitrogen falls to low level.

6. At the end of the extraction (the normal time required for each set of sample for complete lyophilisation is around 2 to 3 hours) release the vacuum slowly and carefully remove the flask containing the sample.

7. Close both ends of the distillation container with stopcocks to prevent atmospheric moisture entering inside and allow to attain room temperature.

8. Add 4 ml of the tissue free water thus collected into 16 ml of the scintillator solution in a vial and count the tritium activity in a liquid scintillation analyser.

The freeze drier is useful when small quantities (up to about 10 g) are to be freeze dried. Liquid nitrogen is poured into thermos flask. The sample in the flask is first frozen by keeping in liquid nitrogen bath, attached to the equipment and vacuum is applied slowly and carefully. The sample gets dried under vacuum at low temperature and distillate gets solidified in the receiver at liquid nitrogen temperature. The modified all glass freeze drier can be left unattended for prolonged periods. The vacuum is continued till the contents of the distilling flask get completely dried.

Alternatively simple vacuum distillation may be substituted instead of freez drying of biological material (fig.1).

NOTE

As a result of the lower vapour pressure of tritiated water vapour, incomplete reactions could offset the results and as such the extraction should be followed to completeness. Some of the organic volatile compounds in the plant tissues inevitably sublime into the trap along with tissue water. Being normally miscible with scintillators, such volatile organic compounds if coloured cause quenching, necessitating a correction procedure while counting TFWT.

3.4.2.2 ESTIMATION OF ORGANICALLY BOUND TRITIUM (OBT)

A combustion procedure is required and described for the quantitative conversion of organically labelled tritium to tritiated water. The procedure is applicable for biological samples including vegetation, foods and tissues.

Carry out the extraction of aqueous tritium fraction procedure (cf. 3.4.2.1b). Repeat the extraction to constant weight of flask (Generally three extractions will

be required). Since such residues are normally hygroscopic, care is taken to prevent HT-H_2O exchange before processing the dry matter for measuring the tissue bound tritium concentration.

The combustion assembly for OBT determination (Fig. 3.2) consists of a 2 litre heavy walled conical flask with a kanthal boat supported from the top by means of two copper rods inserted through a rubber stopper. The rubber cork closes the conical flask air tight. The rods serve as electrical leads for burning the organic matter.

3.4.2.3 PROCEDURE

1. Wrap about 100-150 mg (weighed) of the dry tissue in a cellophane sheet and keep it inside the kanthal boat.

2. Fill the conical flask with oxygen from an oxygen cylinder and close it with the rubber stopper fitted with copper rods and kanthal boat.

3. Keep the flask in a cold ice bath. This will help the condensation of water formed by combustion.

4. Apply a power input of about 60 W for 30 seconds. The contents of the boat will catch flames. If not, repeat the experiment. Incomplete burning can cause colour quenching.

5. Add 20ml of liquid scintillator to the flask. Swirl the flask with scintillator slowly to mix all condensate.

6. Add 18 ml of this scintillator into a counting vial and determine the tritium content by counting in a liquid scintillation analyser. Apply correction for 20 ml scintillator volume.

7. Determine the blank by burning an empty cellophane paper in the flask and repeat the experiment.
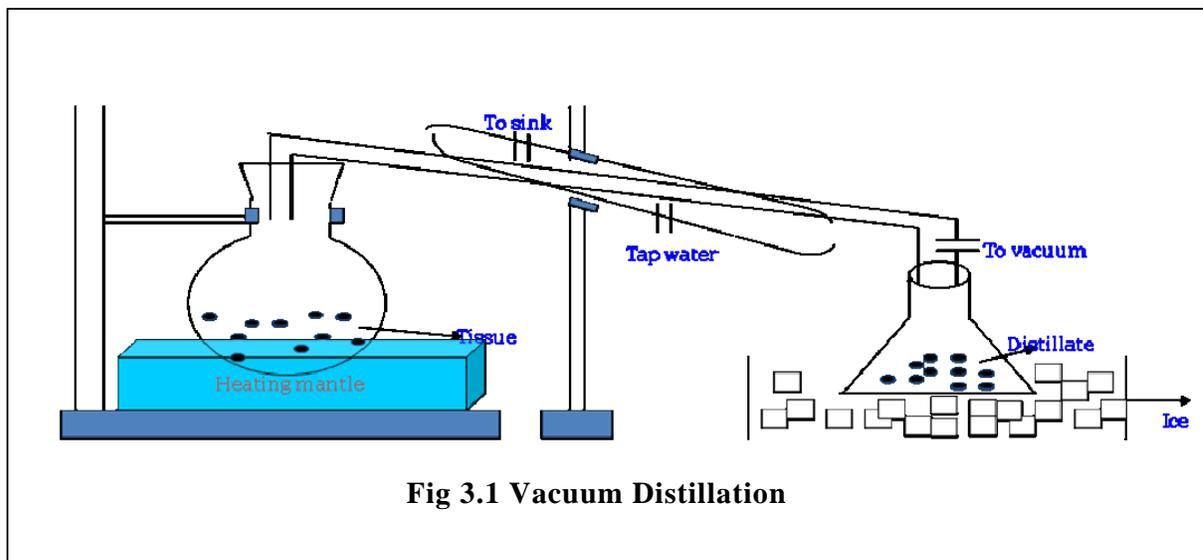
Fig 3.1 Vacuum Distillation

3.5 SEPARATION & MEASUREMENT OF FISSION AND ACTIVATION PRODUCTS IN ENVIRONMENTAL SAMPLES

3.5.1 INTRODUCTION

In addition to fission products like Sr-90, Cs-137 etc activation of stable elements present in structural materials in nuclear reactors give rise to activation products such as ^{134}Cs, ^{95}Zr, ^{95}Nb, ^{51}Cr, ^{54}Mn, ^{63}Ni, ^{106}Ru, ^{60}Co, ^{110}Ag, ^{65}Zn, ^{125}Sb, ^{210}Po, ^{131}I, ^{144}Ce, ^{152}Eu, ^{239}Pu etc. These radionuclides may appear in effluents released to the environment from nuclear power stations and get distributed in various matrices in the environment according to the characteristic behavior of individual nuclide. Except Sr-90, Ni-63 and Pu-239 others are gamma emitters and can be estimated directly by gamma spectrometry. Ni-63 is a low beta emitter with maximum beta energy of 67 keV and is estimated by liquid scintillation counting after radiochemical separation, Sr-90 is estimated by radiochemical separation followed by beta counting and Pu-239 is estimated by alpha spectrometry.

3.5.2 PRINCIPLE

Gamma emitting radionuclides are generally estimated by gamma spectrometry of bulk samples. Separation procedures are however given to analyse very low level of activity. Manganese-54 and Chromium-51, not being beta emitters are estimated by gamma spectrometry only. Cobalt, Nickel and Iron can be separated by anion exchange separation and estimated individually.

3.5.3 REAGENTS

1. Carrier solutions (10 mg/ml) of stable elements of radionuclides to be analysed.
2. HNO_3 Conc. and 4N
3. HCl 8N, 4N, 1N and 0.1 N
4. Dimethyl glyoxime (DMG), 1% solution in absolute alcohol.
5. Oxalic acid (saturated)
6. Ammonium citrate, 5% solution
7. NaOH, 4N
8. Na_2CO_3, 4N

9. NH_4OH, 4N

10. NH_4NO_3 (5%)

11. Na_2SO_3

12. Dowex 1 x 8 (100-200 mesh) anion exchange 10 g resin column , 30 cm X 1 cm dia column

13. Liquid scintillation cocktail or Instagel liquid scintillation cocktail.

3.5.4 PROCEDURE

1. Take the sample (5 g ash of vegetation, organisms etc.,25 g of   soil or silt) in a 500 ml beaker.

2. Add 1 ml of each carrier solutions of the stable elements of those radionuclides   which are to be analysed..

3. Add about 50 ml of Conc. HNO_3 slowly and evaporate to dryness to dehydrate the silica. Repeat the process twice to remove the brown fumes.

4. Extract the residue in the beaker with 50 ml of 4N HNO_3 and filter through Whatman 541. Wash the residue with 4N HNO_3. Collect the washings along with main filtrate in a beaker.

5. Add 4N NaOH slowly till alkaline and then 20 ml 4N Na_2CO_3. Warm and stir the solution. Separate the precipitate by centrifuging and filtration. Discard the filtrate.

6. Dissolve the precipitate in 4N HCl, evaporate to dryness and dissolve the residue in 8N HCl.

7. Prepare a 20 ml column of Dowex - 1 x 8 resin in chloride form, condition with 8N HCl.

8. Pass the 8N HCl sample solution of step 6 through the anion exchange resin column (0.5ml/min) and collect the effluent containing Ni and Mn.

9. Wash the column containing Co and Fe with 60 ml of 8N HCl and collect the washings along with the main effluent fraction and proceed with effluents from step 12 onwards for Ni separation. (Mn-54 and Cr-51 can be estimated by gamma spectrometry of the effluent after evaporating to suitable volume).

10. Elute Co from the column with 50 ml 4N HCl and evaporate to near dryness and subject to gamma spectrometry using a 10 x 10 cm. well type NaI(Tl).

Proceed with eluate from step 20 for Co estimation, if gamma spectrometric system is not available.

11. Elute the column further with 50 ml 0.1 N HCl and collect the eluate containing Fe. Continue from step 24 for analysis of Fe.

12. Add 2 ml of ammonium citrate to the combined effluent solution of steps 8 and 9.

13. Add 5 ml of DMG solution and ammonia solution to precipitate Ni-DMG complex.

14. Filter Ni-DMG, dissolve the precipitate in 4N HCl and reprecipitate Ni-DMG by addition of ammonia solution and DMG. Filter the precipitate and wash with 5% ammonium nitrate solution.

15. Ignite the filter with the precipitate in a tared silica crucible to destroy DMG. Weigh the crucible with the nickel oxide (NiO) and evaluate the chemical recovery of Ni.

16. Convert the Ni-oxide to $NiCl_2$ by adding Conc.HCl and evaporating to dryness. Dissolve the residue in 1N HCl and transfer to a liquid scintillation vial. Evaporate to dryness.

16 (a) Add 1 ml of distilled water to dissolve $NiCl_2$ residue and mix with 15 ml of Instagel solution (3.5.3, 13b) and count in a liquid scintillation analyser. Or

16 (b) Dissolve the residue in alcohol and proceed to step 17.

17. Add a few drops of oxalic acid solution to the alcoholic solution from step 16(b) to precipitate Ni- oxalate, centrifuge and discard the supernatant. Wash the precipitate with alcohol to remove excess oxalic acid. Drain last traces of alcohol, wash once with 5 ml of Dioxane and centrifuge. Discard washings.

18. Add 15 ml of scintillator cocktail (3.5.3, 13a) and 1 g of polystyrene powder and shake well. Keep the vial in dark for an hour until uniform gel is formed and count in a liquid scintillation analyser.

19. From the sample counts subtract the background count, calculate ^{63}Ni activity taking the efficiency determined using standard ^{63}Ni, source prepared in similar liquid scintillation mixture.

Further calculations are similar to ^{3}H in water samples (cf. 3.4.1.4), where V is the quantity of sample taken for analysis.

Standard and blank are prepared as follows:

Ni - oxalate standard:

Evaporate 1 ml Ni-63 standard solution with 1 ml Ni carrier to dryness, dissolve in alcohol and precipitate Ni-oxalate with oxalic acid and proceed similar to the sample (step 17 and 18).

Ni - oxalate blank:

Evaporate 1 ml Ni carrier to dryness, dissolve in alcohol and proceed similar to the standard above.

Ni - Instagel standard:

Evaporate 1 ml Ni-63 standard with 1 ml Ni carrier to dryness, dissolve in 1 ml distilled water and mix with 15 ml Instagel.

Ni - Instagel blank

20. Evaporate 1 ml Ni carrier to dryness, dissolve in 1 ml distilled water and mix with 15 ml Instagel.

21. Evaporate the 4N HCl eluant from step 10 to dryness. Extract the residue with 2 ml 0.1N HCl. Add 100 mg of Na_2SO_3 and warm to precipitate Co-sulphite.

22. Dissolve the sulphite precipitate with a few drops of 1N HCl and add 2 ml of oxalic acid solution. Digest the solution in a water bath for half an hour.

23. Wash the precipitate with distilled water and transfer to a tared filter paper. Dry the precipitate at 90-100°C. Weigh the precipitate as $CoC_2O_4 \cdot 2H_2O$ and count the beta activity.

24. Calculate the ^{60}Co activity using the efficiency of ^{60}Co source similarly prepared.(3.5.5)

25. Evaporate the Fe fraction from step 11 to small volume and transfer the solution to a vial of suitable geometry.

26. Estimate ^{59}Fe activity by gamma spectrometry or alternatively add ammonium hydroxide to the Fe fraction to precipitate $Fe(OH)_3$ and transfer the precipitate to tared filter paper. Dry the precipitate at 90-100 ^{0}C and count in low background beta counter and calculate the ^{59}Fe beta activity.

Note: Many of the environmental matrices contain stable Fe which has to be taken into account while applying the recovery factor for calculation. In the presence of excessive stable Fe, gamma spectrometry alone would give reliable results.

3.5.5 CALCULATION

The Co -60 activity (Bq/kg) in the sample is calculated as follows:

$$[(C/t_1 - B/t_2) \pm 2SD] \times \frac{100 \times 100 \times 1}{E \times Rco \times A}$$

Where,

C=Total count due to sample + background in t_1, secs.

B=Background counts of the counter in t_2 seconds

SD=Standard deviation = $[C/t_1{}^2 + B/t_2{}^2]^{\frac{1}{2}}$

E=Percent efficiency of beta counter

Rco % recovery of added Co carrier

An Aliquot of the sample analysed (kg) equivalent to ash sample taken for analysis.

3.6 SAMPLE PREPARATION AND ANALYSIS OF Sr-89 & Sr-90 IN WATER

3.6.1 INTRODUCTION

Strontium-90 is one of the most important fission products in nuclear fuel cycle. It is present in all environmental samples in trace quantities due to atmospheric weapon testing fallout. Strontium-90 is also present in the low level liquid effluents discharged from nuclear reactors and fuel reprocessing plants. It is a pure beta emitter and its daughter product Yttrium-90 is also a high energy pure beta emitter. Another isotope of strontium namely Sr-89 is also present along with Sr-90 especially in the liquid effluents of power reactors. Procedures for analysis of Sr-89 and Sr-90 in different matrices are briefly described.

3.6.2 REAGENTS

1. Nitric Acid Conc. (AR), 8N, and 4N.

2. Nitric Acid fuming (95%).

3. Calcium carrier (100 mg/ml).

4. Strontium carrier (20 mg/ml).

5. Barium carrier (5 mg/ml).

6. Cesium carrier (20 mg/ml).

7. Ammonium hydroxide (1:1).

8. Ammonium carbonate AR.

9. Acetic Acid (1:1).

10. Sodium chromate solution (25%).

11. Iron carrier (Fe^{+3}) 5 mg/ml.

12. Hydrochloric Acid 4 N.

13. Yttrium carrier (10 mg/ml) standardised.

14. Ammonium oxalate solution (5%).

15. Oxalic Acid solution saturated.

16. Sodium hydroxide AR.

17. Sodium Nitrate AR.

3.6.3 EQUIPMENTS

1. Counting Equipment: Low background beta counting system with background of 1 to 2 cpm and efficiency of 40%. (Gas-flow GM counting system with anti - coincidence circuit and shielding developed).

2. Sintered glass 25 mm filter assembly.

3.6.4 PROCEDURES

3.6.4.1 FRESH WATER

1. Filter about 10 - 30 l of water using whatman 42 filter paper. Acidify the filtered water with Conc. HNO_3 (3ml/l).

2. Add 20 mg Sr, 5 mg Ba, 100 mg Ca and 20 mg Cs carriers.

3. Precipitate hydroxides and carbonates by raising the pH to 10 with 1:1 NH_4OH followed by $(NH_4)_2CO_3$.

4. Stir with electrical stirrer for about 15-30 minutes. Allow the precipitate to settle overnight.

5. Siphon out the supernatant carefully. Centrifuge and wash the precipitate with 1N NH_4OH solution

6. Mix the supernatant to earlier supernatant, preserve for Cs-137 estimation (cf. 3.10.4 step 10).

7. Dissolve the precipitate in 8N HNO_3 and evaporate to dryness. Repeat to dehydrate silica if present.

8. Dissolve the residue in 4N HNO_3 and centrifuge to remove silica.

9. Collect the supernate in a centrifuge tube and evaporate to near dryness under an infrared lamp.

10. Dissolve the content in minimum volume (not more than 5ml) of 8N HNO_3. Cool the centrifuge tube in an ice bath. Add about 30 ml of Conc. HNO_3 (.70%). Stir well, cool for 15 minutes.

11. If the Ca content in the sample is high, do a second Conc. HNO_3 precipitation of Sr after dissolving the nitrate precipitate. (Note: If fuming HNO_3 is available, $Sr(NO_3)_2$ can be precipitated using fuming HNO_3 (95%) and adjusting the HNO_3 concentration to 70%).

12. Dissolve the precipitate in 2 to 5 ml of distilled water and neutralise with ammonia and add 1:1 acetic acid to adjust the pH to about 4-5.

13. Warm the centrifuge tube in a water bath and add 1 ml of sodium chromate solution. Stir well, centrifuge and collect the supernate in another centrifuge tube. Wash the precipitate with distilled water and centrifuge; combine the supernates.

14. Make the combined supernate alkaline using 1:1 ammonium hydroxide and add ammonium carbonate to precipitate $SrCO_3$. Wash precipitate with water. Discard the supernates and washings.

15. Dissolve the precipitate in minimum amount of 4N HNO_3. Heat and allow to boil. Add 1ml Fe carrier and 1:1 ammonium hydroxide dropwise to precipitate ferric hydroxide. Centrifuge and transfer the supernatant to another centrifuge tube. Wash the precipitate with water and add to the earlier supernate. Reject $Fe(OH)_3$. (If floating ferric hydroxide precipitate is observed, filter the supernate solution using Whatman 41 filter paper).

16. To the supernate, add ammonium carbonate to precipitate $SrCO_3$. Digest on a water bath. Centrifuge and discard supernate.

17. Transfer the $SrCO_3$ precipitate to a tared Whatman 42 filter disc in a remountable filter assembly. Wash with water, dry in an oven at 110°C; cool and weigh the filter disc[*] Calculate the weight of $SrCO_3$ recovered .

* The disc has to be kept on a clean aluminium planchet to be used for beta counting and weighed before and after transferring the precipitate.

18. Beta count the $SrCO_3$ on the filter disc to get the total count due to Sr-89 and Sr-90. Using efficiency factor and Sr carrier recovery factor calculate total Sr-89+90 activities (cf. 3.6.5 - 2).

19. Dissolve the $SrCO_3$ precipitate on the filter disc in 5 ml of 4 N HCl and transfer to a centrifuge tube using distilled water for washing. Add 1 ml Y carrier and dilute to about 20 ml. Keep the solution for 14 days for Y-90 build-up to equilibrium level.

20. Heat the centrifuge tube in a water bath to remove CO_2. Precipitate $Y(OH)_3$ by adding 1:1 ammonium hydroxide, centrifuge and wash the precipitate with distilled water. Keep the supernatant and washings, the Sr fraction, for any further verification. Note the time of $Y(OH)_3$ precipitation for the purpose of Y-90 decay correction.

21. Dissolve $Y(OH)_3$ precipitate in 2 ml of 4N HCl and dilute to about 20 ml, heat the solution and add 5 ml of oxalic acid solution and stir to precipitate yttrium oxalate.

22. Centrifuge and discard supernate. Wash Yttrium oxalate once with distilled water. Transfer the precipitate with distilled water to a tared filter disc in the filtration assembly.

23. Dry the Y-oxalate on the filter disc in an oven at 110°C, cool, weigh and count for beta activity in a low background beta counter. Note the time of counting and correct for the Y-90 decay during the time period between initial precipitation (Step-20) and mid time of counting. From the weight of Y-oxalate find the Y carrier recovery factor. Calculate Y-90 activity using efficiency and recovery factors. Sr-90 activity will be equal to Y-90 activity since Y-90 is in secular equilibrium with Sr-90 after 14 days

Procedure B for fresh water can be followed when sequential analysis of a few isotopes is desired especially for large volume samples where duplicate sampling is difficult.

3.6.4.2 SEA WATER

Sea water can be handled similar to fresh water but the main difficulty is that it contains large amounts of Mg & Ca in addition to about 8 mg/l of stable strontium (Ref. NAS 1971). In case of seawater, calcium oxalate precipitation is preferred. The procedure recommended is as follows:

Procedure A:

1. Filter 5-20 l of seawater (depending on the location and activity expected) through Whatman 42 filter paper.
2. Acidify with conc. HNO_3 (3 ml/l).
3. Add Sr, Ba carriers, and warm on a hot plate.
4. Precipitate calcium oxalate by adding saturated oxalic acid followed by ammonium hydroxide to adjust the pH to about 1.
5. Allow the precipitate to settle overnight. Decant the supernatant carefully and centrifuge the calcium oxalate.
6. Wash the precipitate   with 5 % ammonium oxalate solution followed by distilled water.
7. Dissolve the precipitate with concentrated HNO_3 and evaporate with addition of 2-3 ml perchloric acid on a hot plate to decompose the oxalate.
8. Dissolve the residue in 8N HNO_3 and proceed for Sr separation.

Procedure B for sea water can be followed when sequential analysis of a few isotopes is desired especially for large volume samples where duplicate sampling is difficult.

3.7 ALTERNATIVE ESTIMATION OF ^{90}Sr BY CERENKOV RADIATION COUNTING

3.7.1 PRINCIPLE

Light photons in the region of UV-VIS spectrum are emitted whenever the velocity of the charged particle exceeds the speed of light in the medium through which it is passing. The phenomenon of such radiation emission is called Cerenkov effect and the radiations are called Cerenkov radiations. The conventional Liquid Scintillation Analysers can convert the Cerenkov radiation into an electrical signal similar to the one encountered in ^{3}H measurement by liquid scintillation method.

3.7.2 INSTRUMENTATION

A standard Liquid Scintillation Analyser equipped with matched photomultiplier tubes and operating on the principle of coincidence counting technique can be used. The energy of the Cerenkov radiations is in the range of 0-25 keV for ^{90}Y. In a dual channel energy scintillation spectrometer the following energy set up is used.

Channel A: 0 keV - LLD   25 keV - ULD

Channel B: 4 keV - LLD   25 keV - ULD

The ratio of the two channels or the built-in Quench Indicating Parameter like TSIE or SIS can be used to identify the end point energy and the degree of quenching. The background for the Liquid Scintillation Analyser model TRI-CARB 1550 of CANBERRA in region `A' is about 0.1 cps with an efficiency of 50 % for ^{90}Y. The minimum detection limit for ^{90}Y and thus for ^{90}Sr is about 32 mBq for a counting period of 3600 secs.

3.7.3 CERENKOV COUNTING OF EQUILIBRATED ^{90}Sr-^{90}Y.

Liquid samples containing ^{90}Sr activity of the order of 0.1 Bq/l or above can be conveniently counted for Cerenkov radiation to estimate ^{90}Sr concentration. It must be ascertained that the sample is either in equilibrium or allowed to attain equilibrium in-situ in the vial. The daughter product ^{90}Y of ^{90}Sr has beta end point energy of 2270 keV. The beta particles emitted by ^{90}Y are capable of producing Cerenkov radiations with an efficiency of about 50 %. The estimation of daughter product ^{90}Y in an equilibrated sample helps in the estimation of ^{90}Sr. It should be noted that the β energy of ^{90}Sr will not produce Cerenkov radiation efficiently (2

32

% efficiency). This helps in the in-situ estimation of ^{90}Y in the presence of ^{90}Sr and other low energy beta emitters.

A sample volume of about 10-15 ml is taken in a low potassium content LSS vial and counted for about half or one hour duration. The activity levels due to gamma emitters in the sample are estimated by gamma spectrometry using HPGe detector. Count rate due to ^{90}Y is computed as given below:

$$C_{Sr} = CT - \sum_{i=1}^{j} A_i \times F_i \qquad \text{--- (i)}$$

$$Q\,(^{89+90}Sr) = C_{Sr} \times \frac{100}{E} \times \frac{1}{V} \qquad \text{--- (ii)}$$

where   Q = Activity due to $^{89+90}$Sr (Bq/ml.)

        C_{Sr} =   count rate due to ^{89}Sr and ^{90}Y (^{90}Sr) (cps)

        CT =   Total count rate (cps)

        V =   Volume of sample (ml)

        A_i =   Concentration of nuclide (i) in the sample (Bq)

        F_i = Sensitivity factor of nuclide (i) for   Cerenkov radiation (cps/Bq)

        j =   No. of radionuclides

        i =   n th radionuclide.

        E =   % efficiency for Cerenkov radiation.

3.8   SAMPLE   PREPARATION   AND   ANALYSIS   OF   Cs-137   IN ENVIRONMENTAL SAMPLES

3.8.1   PRINCIPLE
3.8.1.1 WATER SAMPLES

Radiocesium along with added Cs carrier is absorbed on ammonium phosphomolybdate(AMP) from acidified water sample. The Cs-AMP is then counting in suitable geometry by gamma spectrometry.

3.8.1.2 BIOLOGICAL SAMPLES

Cesium-137 and added Cesium carrier are equilibrated in solid samples by fusion with fusion mixture or for soluble samples, by digestion of the sample in nitric and hydrochloric acids. Bulk constituents including iron, the alkaline earths and rare earths are removed by leaching the alkali metals from the fusion melt with water or scavenging the acid solution with alkaline carbonate precipitation. Cesium from solution is extracted with AMP. The Cs-AMP is then subjected to gamma spectrometry.

3.8.2 REAGENTS

1. Cesium carrier solution - 10 mg Cs/ml
2. Ammonium phosphomolybdate micro crystals (AMP).
3. Nitric Acid Conc.(AR), 1:1.
4.   Fusion mixture: $NaOH$, $NaNO_3$, Na_2CO_3 anhydrous in the ratio of 5:2:1.

3.8.3 PROCEDURE

3.8.3.1 WATER SAMPLES (SEA WATER, FRESH WATER)

1. Take required amount of filtered water sample (1-50 l).
2. Acidify with Conc. HNO_3 (2ml/litre). Add 1-2 ml of Cesium carrier and stir well.
3. Add 200 mg/l of AMP to the sample and continue stirring for an hour.
4. Allow the AMP to settle and decant off as much as possible of the supernate.
5. The Cesium adsorbed AMP is then subjected to gamma spectrometry.

3.8.3.2 BIOLOGICAL SAMPLES

SAMPLE PREPARATION:

Since Cs is volatile at high temperature wet ashing or acid dissolution is the ideal method of sample preparation. However, this treatment is prohibitive for the size

of sample generally required and dry ashing in most instances is the only practical approach. Loss of Cs is minimised by ashing at temperatures below 450°C and by exposing the samples to elevated temperature for as brief a period as possible. Loss of Cs on ashing is negligible for samples containing sulphate and phosphate. After ashing, grinding and blending, a suitable aliquot of ash is taken for analysis. Different sample types are subjected to preliminary separation to bring them to a common point of analysis.

A. WET ASHING METHOD (For tissue sample)

1. Added 250-500 g of tissue sample in small portions to 500 ml of hot Conc. HNO_3 in 2 l beaker. When all the tissue has been added and the reaction has stopped, add 1ml of cesium carrier solution and other required carriers.

2. Evaporate to approximately 50 ml. If the solution is not clear and oxides of nitrogen are being formed, repeat the evaporation with additional HNO_3.

3. Complete the ashing by the continuous dropwise addition of H_2O_2 and HNO_3.

4. Evaporate gently to dryness to a white residue.

5. Redissolve the residue in 1:1 HNO_3 (25 ml) and transfer to a 400 ml beaker. Dilute to 200 ml with water. With continuous stirring, adjust the pH to 5-6 with NaOH pellets.

6. Add 100 ml of saturated Na_2CO_3 solution with stirring. Stir for 15 minutes more and allow the precipitate to settle.

7. Filter with suction through a whatman 42 filter paper. Wash the precipitate with 10% Na_2CO_3 solution. Reserve the precipitate for Sr or other analysis (where required).

8. Transfer the filtrate and washing to a beaker and cautiously acidify to pH-1 with HCl and add approximately 5-10 ml in excess. Remove dissolved CO_2 by warming.

9. Stir for 15 min. and if any precipitate forms, filter through whatman 42 filter paper wash with hot 1:1 HCl and discard the residue.

10. Transfer the filtrate & washing to a 2 l beaker.

11. Add 200mg AMP, stir for 30 minutes and allow the precipitate to settle.
    Cs-AMP is then counted for radiocesium activity using gamma spectrometry.

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B. DRY ASHING METHOD

1. Weigh 1-3 kg of the sample. (food crops, vegetables, milk, fish and other aquatic food organisms.)

2. Dry the sample at 110^0C for 24 to 48 h. and weigh.

3. Take the dry sample for gamma counting in a suitable geometry. If the activity is low proceed with step 4.

4. Ash the sample at 450^0C (48 h)

5. Cool and weigh the ash and take for gamma counting in suitable geometry. If the activity is low proceed with the radiochemical separation for Cs.

6. Carry out initial mobilisation of cesium from the ash of biological samples byeither by. Alkali fusion method or Acid leaching method as detailed below.

i. Alkali Fusion Method:

1. Weigh 3 to 5 g (or 20 g for near background samples) of the dry ash of the biological sample and take in a 100 ml capacity Nickel/S.S. crucible. Add 1 ml of Cs carrier and dry under infra-red lamp.

2. Add about 10 to 15 g fusion mixture to the crucible and fuse the content over a burner till a clear liquid melt is obtained. Heat further for about 10 minutes. Allow the melt to cool thoroughly.

3. Soak the contents with 50 ml distilled water and digest. Break the lumps slowly. Transfer the contents into a 400 ml beaker quantitatively with distilled water.

4. Break any lumps of fused mass further with a glass rod and digest for 15 minutes over a flame.

5. Filter the contents through whatman 41 filter paper. Wash with distilled water. Collect the filtrate and washings for Cs estimation.

6. Acidify slowly the filtered solution with 1: 1 HNO_3 and heat to remove CO_2.

7. Add 200 mg/l of AMP and stir for 30 minutes. Proceed for gamma spectrometry.

ii. Acid Leaching Method.

1. Weigh 3 to 5 g of dry ash (20 g for near background samples) of biological sample in a 400 ml beaker

2. Add 1ml of Cs carrier.

3. Add measured volume (30-60 ml) of Conc. HNO_3 to the ash sample and evaporate to dryness.

4. Repeat step 3 twice and dry till brown fumes are removed. If the residue is still brown, add 10 ml HNO_3 and a few drops of $HClO_4$, cover with a watch glass, heat to boil and finally remove white fumes by low heating on hot plate.

5. Add measured volume (5 to 20 ml) of Conc. HCl and evaporate to dryness

6. Extract the residue with 30 ml of hot 1:1 HCl thrice, centrifuge and collect the supernatant solution.

7. Add 30 ml of 0.1 N HCl to the residue stir well and collect the supernatant and mix with the solution in step 6. Discard residue if any.

8. Add 6 N NaOH to the solution till it becomes alkaline and then 10 ml of saturated sodium carbonate solution and centrifuge and wash the precipitate with distilled water.

9. Collect the supernatant and washings. Acidify the solution slowly with 1:1 HNO_3 and heat to remove CO_2.

10. Add 200 mg/l AMP and stir for 30 minutes. Proceed for gamma spectrometry.

3.8.4 CALCULATIONS

The Cs -137 activity (Bq/l or kg) in the sample is calculated as follows:

$$[(C/t_1-B/t_2) \pm 2SD] \times \frac{100 \times 100 \times 1}{E \times Rcs \times A}$$

Where, C= Total count due to sample + background in t_1, secs.

B=Background counts of the counter in t_2 seconds

SD=Standard deviation = $[C/t_1^2 + B/t_2^2]^{\frac{1}{2}}$

E=Percent efficiency of beta counter, Rcs % recovery of added Cs carrier

A=Aliquot of the sample analysed (kg or litre).

3.9 ESTIMATION OF Sr-89, Sr-90 AND Cs-134+137 IN BIOLOGICAL SAMPLES

3.9.1 PRINCIPLE

Ash of biological samples such as food crops, vegetables, milk, fish and other aquatic food organisms is fused with fusion mixture after addition of Cs and Sr

carriers. The fused mass is extracted with distilled water. Cs carrier along with $^{134+137}$Cs will get extracted with water and Sr carrier with $^{89+90}$Sr will remain in the insoluble carbonate residue.

Aqueous extract containing Cs is acidified with nitric acid and Cs is collected by replacement of ammonium ions on ammonium phosphomolybdate(AMP). Cs-AMP is dissolved in ammonia and gamma counted or Cs.

The carbonate residue is dissolved in nitric acid. Sr is separated from Ca using fuming HNO_3 or conc.HNO_3 in cold condition. Ba, Ra and Pb activities are removed by Ba-chromate scavenging. Ferric hydroxide scavenging of Sr solution removes all other fission products including ^{90}Y, daughter product of ^{90}Sr. ^{89}Sr and ^{90}Sr can be estimated individually after ^{90}Y separation. Yttrium carrier is added to Sr solution and kept for 14 days for growth of ^{90}Y. Y-90 is precipitated as hydroxide and then as oxalate. Y-oxalate is beta counted and ^{90}Sr is evaluated from ^{90}Y counts. Chemical recoveries are corrected for by using Sr and Y carrier recoveries. Sr-89 activity is calculated by subtracting ^{90}Sr activity from the total $^{89+90}$Sr activity or alternatively by solving simultaneous equations formed from the two countings done before and after growth of ^{90}Y.

Prior to radiochemical separation, gamma spectrometry of the sample is carried out for gamma emitters. However, for beta emitters radiochemical separation is necessary.

3.9.2 REAGENTS

1. Nitric Acid Conc. (AR), 8N, 4N
2. Hydrochloric Acid 4N
3. Acetic Acid 1:1
4. Ammonia solution (AR) (sp. gr. 0.91)
5. Ammonium Phospo Molybdate (AMP)
6. Ammonium Carbonate. A.R
7. Sodium Chromate solution (25%)
8. Oxalic Acid solution (10%)
9. Cesium carrier (10 mg Cs/ml) as CsCl or $CsNO_3$ (standardised)
10. Strontium carrier (20 mg Sr/ml) as nitrate (standardised)
11. Yttrium carrier (10 mg Y/ml) as nitrate (standardised)

12. Barium carrier (5 mg Ba/ml) as nitrate

13. Iron carrier (Fe^{3+}) solution (5 mg Fe/ml) as nitrate

17. Fusion mixture: $NaOH+NaNO_3+Na_2CO_3$ anhydrous in the ratio of 5:2:1

3.9.3 EQUIPMENTS

1. Counting Equipment: Low background beta counting system with background of 1 to 2 cpm and efficiency of 40%. (Gas-flow GM counting system with anticoincidence set up) and gamma spectrometry system.

3.9.4 SAMPLE PREPARATION

1. Weigh 1-3 kg of the sample. (food crops, vegetables, milk, fish and other aquatic food organisms.)

2. Dry the sample at 110^0C for 24 to 48 h. and weigh.

3. Take the dry sample for gamma counting in a suitable geometry. If the activity is low proceed with step 4.

4. Ash the sample at 450^0C (48 h)

5. Cool and weigh the ash and take for gamma counting in suitable geometry. If the activity is low proceed with the radiochemical separation for Cs and Sr.

6. Carry out mobilisation of cesium and strontium from the ash of biological samples by A. Alkali fusion method, or B. Acid leaching method as detailed below.

A: Alkali Fusion Method:

1. Weigh 3 to 5 g (or 20 g for near background samples) of the dry ash of the biological sample and take in a 100 ml capacity Nickel/S.S. crucible. Add 1 ml of Cs, Sr, Ba carriers and dry under infra-red lamp.

2. Add about 10 to 15 g fusion mixture to the crucible and fuse the content over a burner till a clear liquid melt is obtained. Heat further for about 10 minutes. Allow the melt to cool thoroughly.

3. Soak the contents with 50 ml distilled water and digest. Break the lumps slowly. Transfer the contents into a 400 ml beaker quantitatively with distilled water.

4. Break any lumps of fused mass further with a glass rod and digest for 15 minutes over a flame.

5. Filter the contents through whatman 41 filter paper. Wash with distilled water. Collect the filtrate and washings for Cs estimation. Take the precipitate on filter paper for Sr estimation (step 8).

6. Acidify slowly the filtered solution with 1: 1 HNO_3 and heat to remove CO_2.

7. Add 200 mg/l of AMP and stir for 30 minutes. Carry out the gamma spectrometry to evaluate Cs-134 & cs-137.

B: Acid Leaching Method.

1. Weigh 3 to 5 g of dry ash (20 g for near background samples) of biological sample in a 400 ml beaker

2. Add 1ml of Cs, Sr and Ba carriers.

3. Add measured volume (30-60 ml) of Conc. HNO_3 to the ash sample and evaporate to dryness.

4. Repeat step 3 twice and dry till brown fumes are removed. If the residue is still brown, add 10 ml HNO_3 and a few drops of $HClO_4$, cover with a watch glass, heat to boil and finally remove white fumes by low heating on hot plate.

5. Add measured volume (5 to 20 ml) of Conc. HCl and evaporate to dryness. (About 1ml per gram of ash is required to remove HNO_3 fumes completely).

6. Extract the residue with 30 ml of hot 1:1 HCl thrice, centrifuge and collect the supernatant solution.

7. Add 30 ml of 0.1 N HCl to the residue stir well and collect the supernatant and mix with the solution in step 6. Discard residue if any.

8. Add 6 N NaOH to the solution till it becomes alkaline and then 10 ml of saturated sodium carbonate solution and centrifuge. Proceed with the supernatant for Cs separation.

9. Dissolve precipitate with 1:1 HNO_3 and proceed for determination of Sr

10. Collect the supernatant from step 8 Acidify the solution slowly with 1:1 HNO_3 and heat to remove CO_2.

11. Add 200 mg/l AMP and stir for 30 minutes. Carry out the gamma spectrometry to evaluate Cs-134 & cs-137.

3.9.5   CALCULATION

Sr-90 activity: (Bq/g fresh sample) :

$$N(\text{Sr-90}) = [(C/t_1 - B/t_2) \pm 2SD] \times \frac{100 \times 100 \times 100 \times A}{E \times F_1 \times F_2 \times R_{sr} \times R_y \times W \times 100}$$

C = Total count due to sample Y-90 + Background in time t_1 secs

B = Background count in time t_2 secs.

SD = Standard deviation $\pm [C/t_1^2 + B/t_2^2]^{1/2}$

E = Percent efficiency of the beta counter for Y-90.

F_1 = Y-90 growth factor (< 1)

i.e. $[1-\exp(-\lambda\ tg\ ]$ where, λ is the decay constant for Y-90 and tg is the period   of Y-90 growth. (for 14 days period F_1 can be taken as 1)

F_2 = Y-90 decay factor

i.e. $\text{Exp}(-\lambda\ td)$ where λ is Y-90 decay constant and td is the decay period between precipitation of $Y(OH)_3$ and mid point of counting of Y-oxalate.

(λ for Y-90 is 1.083×10^{-2} hrs^{-1})

R_{sr} = Percent recovery Sr carrier

R_y = Percent recovery of Y carrier

W = Weight of sample ash taken for analysis

A = Percentage ash for the sample w.r.t fresh wt.

3. Sr-89 Activity: (Bq/g fresh sample)

Sr-89+90 activity in Bq/g is calculated (N Total Sr-89+90) from the total Sr counted immediately after Y-90 removal by $Fe(OH)_3$ precipitation as follows(cf.3.6.4.1 Step18).

$$N(\text{Sr-89+90}) = [(C/t_1-B/t_2) \pm 2SD] \times \frac{100 \times 100 \times A}{E \times R_{sr} \times W \times 100}$$

C, B, SD, E, R_{sr}, W and A are similar to what is given for Sr-90 but refer to total Sr counting.

Sr-89, is calculated as

$N_{Sr-89} = N_{Sr-89+90} - N_{sr-90}.$

3.10 DETERMINATION OF NATURALLY OCCURING RADIONULIDES

3.10.1 INTRODUCTION

The natural activity in the environmental samples is mainly due to K-40, and U-238 and Th-232 radioactive series. The gamma emitting radionuclides of radioactive series are conveniently determined by using gamma spectrometry. The samples are processed and sealed in air tight containers for a period of one month to ensure radioactive equilibrium between parent and daughter products of the natural series. However, the estimation of Po-210, Ra-226 and Ra-228 is estimated by radiochemical separation.

3.10.2 DETERMINATION OF POLONIUM -210

BIOLOGICAL SAMPLES PREPARATION:

PRINCIPLE

Since Polonium is volatile at high temperature wet ashing or acid dissolution is the ideal method of sample preparation. However, this treatment is prohibitive for the size of sample generally required and dry ashing in most instances is the only practical approach. Loss of polonium is minimised by ashing at temperatures below 450°C and by exposing the samples to elevated temperature for as brief a period as possible. Loss of Polonium on ashing is negligible for samples containing sulphate and phosphate. After ashing, grinding and blending, a suitable aliquot of ash is taken for analysis. Different sample types are subjected to preliminary separation to bring them to a common point of analysis.

A. WET ASHING METHOD (For tissue sample)

1. Add 250-500 g of tissue sample in small portions to 500 ml of hot Conc.
2. HNO_3 in 2 l beaker. When all the tissue has been added and the reaction has stopped, add 1 ml of Po-208 tracer (2dpm).

3. Evaporate to approximately 50 ml. If the solution is not clear and oxides of nitrogen are being formed, repeat the evaporation with additional HNO_3.

4. Complete the ashing by the continuous dropwise addition of H_2O_2 and HNO_3. Evaporate gently to dryness to a white residue. Dissolve the residue in 250 ml 0.5 M HCl

5. Add 200 mg ascorbic acid

6. Proceed for Po-210 plating as per the procedure given under polonium plating procedure.

B. DRY ASHING METHOD

1. Weigh 10-20g of the dry sample (food crops, vegetables, milk, fish and other aquatic food organisms.) and take in a 250 ml round bottom flask.

2. Add slowly about 50 ml of 8N HNO_3 & allow the reaction to subside and evaporate to dryness Add 1 ml of Po-209 (about 2 dpm) tracers.

3. Connect the flask for refluxing with a 45 cm water condenser. Reflux the dry mass with 8N HCl for 2 hours and allow to cool. Centrifuge and collect the supernatant solution and evaporate to near dryness. Take the residue in a beaker and dissolve it in about 250 ml 0.5N HCl. Add 200 mg ascorbic acid.

4. Proceed for Po-210 plating as per the procedure given under polonium plating procedure.

C. WATER SAMPLE PREPARATION

PRINCIPLE

Polonium can be coprecipitated with ferric hydroxide in large volume of water samples. The ferric hydroxide is dissolved in 0.5M HCl and Po-210 can be deposited electrochemically on silver plate.

1. Take about 10 liters of filtered (Whatman 42) water sample and add ^{209}Po tracer (about 2dpm) each.
2. Add 150 mg of iron carrier as iron chloride or nitrate, stir well.
3. Add 1: 1 NH_4OH slowly to raise the pH to 9 with continuous stirring for two hours.
4. Allow the precipitate to settle down for overnight.
5. Decant off the supernatant solution.
6. Centrifuge the remaining solution and collect the precipitate.
7. Dissolve the precipitate in 250 ml 0.5 M HCl
8. Add 200 mg ascorbic acid and proceed for Po-210 plating as per the procedure given for soil and sediment.

D. PROCEDURE FOR POLONIUM PLATING

1. Take the sample from the step proceed for polonium plating i.e. extracted sample in 250 ml 0.5NHCl. Keep the beaker on a hot plate cum magnetic stirrer.
2. Take a clean and washed silver planchet and count its both the sides separately for alpha activity background in the Po-210 region using a calibrated alpha spectrometer.
3. Dip the silver planchet (by hanging from outside) in the above solution and allow the stirring for about 2 hours at constant temperature of 60^0C.
4. After two hours the plate is removed and washed by running water. Dry the silver planchet and count its both the sides separately using a calibrated alpha spectrometry system to evaluate Po-210 activity in the sample.
5. Po-210 can be estimated by alpha spectrometry. Calculate the activity of Po-210 (5.305 MeV) with respect to the added Po-209 (4.88 MeV) tracer activity

CALCULATION

The Po-210 activity (Bq/l or kg) in the sample is calculated as follows:

$$[(C/t_1 - B/t_2) \pm 2SD] \times \frac{100 \times 100 \times 1}{----------------}$$

$$E \times Rpo \times A$$

Where, C Total counts due to sample + background in t_1, secs.

B   Background counts of the counter in t_2 seconds

SD   Standard deviation = $[C/t_1{}^2 + B/t_2{}^2]^{\frac{1}{2}}$

E   Percent efficiency of beta counter, Rcs   % recovery of added Po carrier

A   Aliquot of the sample analysed (kg or litre).

2.10.3 DETERMINATION OF Ra-226 AND Ra-228 and POLONIUM -210

Principle

Radium is co-precipitated along with barium sulfate and purified $^{226+224}$ Ra is counted for α activity using silver activated zinc sulphide. α- counter, while 228 Ra being a β-emitter is allowed to decay into ^{228}Ac till a secular equilibrium is reached. β-activity due to ^{228}Ac is then counted using a G. M. counter.

$^{226 + 224}$ Ra

Reagents

Concentrated Nitric Acid, Barium Carrier, lead carrier, sulfuric acid Ethylene diamine tetra acetic acid, Glacial Acetic acid.

1. Take suitable amount (4 ltr. Approx. for low level) of water sample or acid extract of soil.
2. Evaporate to dryness.
3. Dissolve the residue in 5 to 10 ml conc. Nitric acid. And again evaporate to dryness. Repeat 2-3 times to bring the sample in nitrate form.
4. Dissolve the residue in water and add 2.5 mg of Ba carrier and 200 mg lead carrier.
5. Precipitate sulfates with 1:1 sulfuric acid. Centrifuge and discard the supernate.
6. Dissolve the precipitate in 10% ammonical EDTA solution while keeping on a water bath.
7. Add glacial acetic acid and precipitate only Barium sulfate.
8. Centrifuge and discard the supernate containing lead.
9. Repeat the steps 6 to 8 to remove any traces of lead.
10. Take background α-counts of a washed dried and pre-weighed stainless steel disc.
11. Transfer the precipitate onto the disc with minimum amount of distilled water.

12. Dry under and infra red lamp. Fire on a burner flame and cool.

13. Count α - activity due to $^{226+224}$Ra.

14. Count the reference standard for converting counts per second to disintegration per second.

15. Find the recovery of Ba-carrier.

Calculations

α-activity due to $^{226+224}$Ra = net cps x 100/efficiency x 100 / Recovery of Ba

x 1/Volume or weight

^{228}Ra

Reagents

Concentrated Nitric Acid, Barium Carrier, lead carrier, sulfuric acid Ethylene diamine tetra acetic acid, Glacial Acetic acid, perchloric acid, bismuth carrier, hydrofluoric acid, hydrochloric acid

Procedure

1. Take the precipitate of Radium Barium sulfate from step 7 in centrifuge tube.

2. Add 5 mg Lanthanum carrier, 100mg lead carrier and 5 mg Bismuth carrier.

3. Dry under an infra red lamp.

4. Keep for 30 hours at room temperature for attainment of secular equilibrium between Radium and Actinium.

5. Dissolve the residue in concentrated perchloric acid by heating the centrifuge tube slowly and cautiously.

6. Add 1:1 Sulfuric acid centrifuge and discard the precipitate containing lead, barium and radium.

7. To the supernate add 2 to 3 ml conc HF followed by a few drops of HCl. Centrifuge and discard the supernate.

8. Wash the Lanthanum Fluoride precipitate with HF + HCl washed solution

9. Transfer the precipitate on a washed dried precipitate on a weighed aluminium planchet.

10. Dry under infra red lamp.

11. Count β-activity due to ^{228}Ac corresponding to ^{228}Ra using G. M. Counter and note the time.

12. Take background and reference standard counts also as described earlier.

Calculations

β-activity due to ^{228}Ra = net cps x 100/efficiency x 100 / Recovery of Ba

x 1/Volume or weight x e $^{0.693\ t/\ half\ life}$

t is the time between separation and counting between step

4) RADIOACTIVITY MEASUREMENTS AND NUCLEAR COUNTING INSTRUMENTATION

4.1 INTRODUCTION

The radioactivity contents in different environmental matrices are measured by using nuclear instruments. In this section, the principle, methodology, calibration and performance of different detector systems have been described.

4.2 COUNTING SYSTEMS

The most common counting systems used in nuclear research laboratory are:

i) Beta Counting System   ii)   Alpha Counting System iii) gamma Spectrometry

4.2.1 BETA COUNTING SYSTEMS

4.2.1.1 GM COUNTING SYSTEM

Beta counting systems generally utilise a medium sized sealed normal type or low background type of end window Geiger-Muller tube as detector. Argon as counting gas and halogens or organic gas as quenching gases is used in these tubes. Beta particles incident in the gas volume through a mica window (10 mg/cm^2) dissipate their energy in ionising the gas atoms. Electrons produced in the process are swept to anode and are collected. The signal is quite strong as the detector is operated in G.M. region and does not require complicated electronics. An electronic quench unit (paralysis unit) collects these electrons and provides a measurable pulse. It also provides a selectable fixed dead time of 250 or 350 or 550 micro sec.

Beta counting system can be assembled by utilising nuclear instrumentation modules like EHT unit, Paralysis unit, timer / scalar and the power supply bin. Stand alone systems are also available which contain electronic circuitry to provide required functions of the above units.

CALIBRATION

Analytical grade potassium chloride crystals are powdered after drying at 110 ^{0}C for 1 hour and uniformly spread and fixed with gelatin or collodion in an aluminum planchet. The size of the planchet is properly chosen to match the detector and

window size. Strength of around 2 Bq of K-40 is sufficient to give significant count rate. Natural potassium contains about 0.012% of K-40. Higher strengths will increase the thickness of standard source causing self absorption. The efficiency of the detector is mostly independent of energy in G-M mode of operation but attenuation due to sample thickness needs to be corrected. Gas filled GM counters normally gives 15-20 % efficiency and about 0.4 cps (counts per second) background. The specific activity of KCl is 16 Bq/g.

BACKGROUND

The background due to cosmic radiation and environmental radiation is reduced to some extent by employing good quality lead shielding of about 5 cm thickness with Al or Cu lining. Background radiation of detector materials cannot be reduced and therefore detectors giving low background should be chosen. Detector of size 25 mm x 50 mm (dia x height) would have background in the region of about 15 cpm to 50 cpm in 5 cm Pb shielding depending on the type of detector.

4.2.1.2 GAS FLOW BETA COUNTER USING ANTI COINCIDENCE TECHNIQUES

Generally two or three GM counters of either planar or spherical shape namely main counter or guard counter are used. The counters are mechanically arranged in such a way that background radiation due to cosmic rays and surrounding materials do not interact directly with the medium of main counter where the sample is placed without passing through the guard counters. The counters have an aluminum or gold foil window of about 1.0 mg/cm^2 through which the β particles traverse and reach the gas (Argon) chamber with isopropyl alcohol vapours and ionise the medium. The signals from both counters are collected through the anode wire.

PRINCIPLE

The electronic signals from both main and guard counters are fed to an anticoincidence electronic unit. The unit filters out the signal of main counter if it has a corresponding signal of the guard output in coincidence within a specified resolving time. Resolving time depends on the electronic unit used and the associated

detector and electronics. It varies from 50 msec to 200 msec. Anticoincidence signals from the main counter alone are fed into the scaler and recorded.

PERFORMANCE

Due to anticoincidence technique and shielding the background of the system is reduced to about 1-2 cpm. The efficiency of the counter is generally independent of incident beta particle, once the particle enters the chamber. However, due to absorption of energy of incident particle by the window material the efficiencies get affected for different energies. The efficiency for ^{40}K is approximately 40%. The efficiency for other beta energies of ^{137}Cs and ^{90}Sr is about 35%. The efficiency is also influenced by the thickness of sample. The efficiency for ^{90}Y is about 45%. The MDL (3σ) of low background beta counting system is 0.023 Bq for 3600 s counting duration.

4.2.2 ALPHA COUNTING SYSTEM

An alpha counting system comprises of an alpha probe and counting electronics including high voltage   supply to probe, a preamplifier, amplifier, timer and scaler.

ALPHA PROBE

Alpha probe consists of a scintillator detector made up of a thin layer of silver activated zinc sulphide [ZnS(Ag)] crystal and a high performance low noise photomultiplier tube(PMT). The density of the crystal is about 10 mg/cm^2. The PMT and crystal are placed in a light tight steel housing so as to have very low background of the order of about 1.0 x 10^{-3} cps at an efficiency of about 30%. The operating voltage is usually less than 1500 V enabling the use of simple scalers.

PRINCIPLE

Alpha particles incident on the ZnS (Ag) powder spend their energy completely in raising the valence electrons into the conduction band. The electrons from the excited state return to ground state either directly or through activator sites. The loss of energy appears as visible/UV light rays when they reach ground state. Cathode of PMT is positioned in such a way that it absorbs full light energy and emits primary

electrons. PMT multiplies the primary electrons and develops a current signal at the output of anode which is amplified and shaped to register it in a counter.

PERFORMANCE

The background of the system is about 0.002 cps and the efficiency for plated ^{239}Pu source is 25% to 30 %. The efficiency is largely influenced by the thickness of sample. MDA (3σ) for unit volume of sample is 0.0075 Bq for a counting time of 5000 s.

4.2.3 ESTIMATION OF ALPHA OR BETA ACTIVITY

Counter efficiency:

$$S = \left(\frac{N_a}{t_1} - \frac{N_b}{t_2}\right) \times \frac{100}{Q}$$

   S   - Efficiency of the counter in percentage.

   N_a - Gross counts due to standard in time t_1 secs.

   N_b - Background counts in time t_2 secs.

   Q   - Source strength in dps (Bq)

 Sample activity estimation:

$$A = \left(\frac{N_a}{t_1} - \frac{N_b}{t_2}\right) \times \frac{100}{S} \times \frac{1}{V} \times \frac{1}{Y}$$

   A   - Activity of the sample in Bq/g or Bq/ml.

   N_a - Gross counts due to sample and background in t_1 secs.

   N_b -   Background counts in t_2 secs

   S   -   Efficiency of counter

   V   - Volume/weight of the sample

   Y   - Chemical yield fraction (< 1)

Error estimation:

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$$ s = 2 \text{ x } \left[\frac{N_a}{t_1{}^2} + \frac{N_b}{t_2{}^2} \right]^{\frac{1}{2}} \text{ x } \frac{100}{S} \text{ x } \frac{1}{V} \text{ x } \frac{1}{Y} $$

s - Standard deviation at 95% confidence.

4.3 RADIATION SPECTROMETRIC SYSTEMS

Spectrometry is a system of several devices which helps in identification and estimation of mostly gamma or alpha emitting radionuclides. It broadly comprises of a detector, a high voltage unit, signal shaping electronics and multichannel analyser.

The spectrometry can be divided into three categories.

i)   Gamma Spectrometry

ii) Alpha Spectrometry

iii) Beta spectrometry

Gamma spectrometry is a non destructive technique used to identify and quantify gamma emitting radionuclides. It is mainly carried out using NaI(Tl), or high purity Germenium (HPGe) detectors for gamma energies primarily in the range of 100 keV to 3 MeV. Thin crystals of both types are used for low energy gamma emitter analysis.

The following paragraphs describe the theory of detectors and their characteristic parameters used in gamma spectrometry.

4.3.1 SCINTILLATION DETECTORS

4.3.1.1 INTRODUCTION

The materials which produce light flashes when ionising radiation passes through them are called scintillators. Scintillators exist in three physical states viz. solid, liquid and gases but the first two are most widely used.

A scintillation counter consists of a scintillator which produces light flashes due to the interaction of ionising radiation. The scintillator is optically coupled to a high gain, low potassium and low noise photomultiplier tube which convert the incident light photons into an electrical pulse.   The magnitude of electrical pulse is

proportional to the intensity of light flash. The output of the detector system is proportional to the energy of the incident radiation.

The important features of a scintillation detector are:

a) Light output is proportional to the incident energy which enables direct measurement of particle energy.

b) Majority of the scintillators have high density and hence high stopping power.

c) They have short decay time in the range of 10^{-6} to 10^{-9} secs.

d) The detectors can be fabricated in variety of shapes and sizes.

The scintillation detectors are broadly divided into two categories

(i)   Inorganic Scintillators.

(ii)   Organic Scintillators.

4.3.1.2 INORGANIC SCINTILLATORS

These scintillators (crystals) are alkali halides containing small quantities of impurity as activators. The principle behind the light photon generation is either excitation or ionisation of electrons from valance band by the incident energetic photon or charged particle. The return of electron to the valence band produces the light photon. The light photon is further processed by PMT to produce an electrical signal which is later amplified and analysed by the sophisticated electronics. The commonly used inorganic crystals are NaI(Tl), ZnS(Ag), CsI(Tl), BGO, Phoswich detectors and BF_3.

NaI(Tl) : The crystal material is hygroscopic and will deteriorate due to water absorption if exposed to air for long time. Therefore the detectors are made air tight by suitable canning material and are available in various sizes. The resolution of a 3" x 3" detector at 662 keV is about 7%. This type of detector is one of the most widely used for gamma spectrometry purpose.

4.3.1.3 LIQUID SCINTILLATOR SOLUTIONS

These are organic solutions with the sample incorporated in to the medium and have the advantage of filling into any container and obtain a large size detector medium. This usually would have very high sensitivity. The scintillator solutions consist of 3-4 substances namely primary solvent, secondary solvent, primary solute and secondary solute along with solubilisers. Solvent material acts as stopping medium for radiation/particle while solute substance produces light photon. Secondary solute

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acts as wave length shifter to provide increased photocathode efficiency. As high as 100% efficiency could be obtained for ^{14}C using this scintillator medium. Commonly used solvents are Toluene, P-Xylene and Dioxane and solutes are PPO and P-Terphenyl and the secondary solute are POPOP or Bis. methyl/styryl/benzene (Bis. MSB). Organic scintillator solutions are generally used for beta counting and beta spectrometry of low energy beta emitters.

4.3.2 SEMICONDUCTOR DETECTORS

The detectors manufactured from the materials whose conductivity lies between the good conductors and insulators are called semiconductor detectors. The conductivity of an inorganic crystal depends on the energy gap between the valance and conduction bands. It is almost 0 for good conductors (Graphite) and 6 eV for diamond (insulator). The materials Ge & Si are classed as semiconductors because the energy band gaps are 0.7 eV and 1.1 eV respectively. These two semiconductors are most widely used in radiation measurements.

ENERGY CALIBRATION

Energy calibration of NaI(Tl) detector is performed by using sources like ^{137}Cs and ^{60}Co. For lower energies ^{192}Ir and ^{108m}Ag can be used. Sources should be chosen in such a way that they have long half-lives and are mono energetic or have multiple energies of wide separation. Initially, after setting up of the spectrometer, place the ^{137}Cs source and acquire spectrum. Note the peak position due to ^{137}Cs source. If the peak is not in the desired position, increase or decrease the gain of the linear amplifier and obtain the peak at desired position. For example if a 10 keV/channel calibration is required, the peak should be positioned at 66th channel for 662 keV gamma line of ^{137}Cs. Now place different sources of known energies one by one and note their channel positions. Make a table containing various gamma energies and corresponding channel positions and draw a linear graph.

A linear equation of $y = mx + c$ or $E = m(ch) + c$ can be easily fitted. The equation can later be used to find the energy of unknown peak channel.

EFFICIENCY CALIBRATION

The geometry in which the samples are analysed should be ascertained and in the same reproducible geometry the spectrometric system should be calibrated for its

overall sensitivity. Sources obtained from recognised laboratories mostly in liquid form are to be filled into container of selected geometry after suitable dilution. Spectrum should be acquired until sufficient number of counts is registered in the peak region.

$$S \% = \frac{Ar}{LT} \times \frac{100}{C} \times \frac{100}{A}$$

S % = Efficiency at a given energy.

Ar = Area under the peak.

C = Source strength in Bq(dps).

A = Gamma abundance of radionuclide (No. of gamma per 100 disintegration)

LT = Live time in secs.

Long lived gamma sources like ^{137}Cs, ^{60}Co, ^{192}Ir, ^{108m}Ag and ^{54}Mn can be used to calibrate the system for various gamma energies. A plot of energy versus efficiency is to be drawn for a particular geometry which can be used for other energies for which a standard source may not be available.

RESOLUTION OF DETECTOR

A good spectrometric system containing all integral assembly of NaI(Tl) detector has a resolution of about 7.0 % at 662 keV gamma line of ^{137}Cs. Resolution is expressed as full width at half maximum (FWHM) of a peak in % of energy.

The resolution is calculated as

$$FWHM \% = \frac{\delta C \times Fe}{E} \times 100$$

δC = Width in channels at half height of maximum peak counts.

Fe = Energy calibration factor (keV/ch)

E = Energy of gamma line (keV).

4.4 GAMMA SPECTROMETRY WITH HPGe DETECTOR

4.4.1 INTRODUCTION

Intrinsic or hyperpure Germanium detectors (HPGe) are most widely used for high resolution gamma spectrometric purpose. They can be used for both low level and high level samples of different geometries. The instrumentation and principle of detection are the same as of NaI(Tl) detector.   The difference is that the semiconductor detector (HPGe) has high resolving capacity by which it can differentiate the photo peaks due to two gamma emitting nuclides of near by energies better than NaI(Tl) detector.

4.4.2 INSTRUMENTATION

The detector, which is generally 50 - 130cc or higher in volume, needs liquid nitrogen for cooling during operation. The detector is mounted vertically or sideways on a cryocan of 26-30 liter capacity which is filled with liquid nitrogen. The cryocan is kept on a balance to monitor the level of liquid nitrogen. On an average the loss rate of liquid nitrogen is about 1kg/d at 25°C temperature. The cryocan of the detector has to be filled regularly with liquid nitrogen. Suitable delivery system has to be fabricated and kept ready. Stock of liquid nitrogen is stored in separate cryocans of 40 - 55 litre capacity. During the initial setting up of the detector care should be taken so that a minimum cooling of 6 hrs or preferably overnight is necessary before applying bias voltage to the detector.

4.4.3 SETTING UP OF INSTRUMENTS

Connect all the cables of the system to respective units which are marked on multichannel analyser. Before applying the bias ensure that liquid nitrogen level is maintained in the cryostat. If the liquid nitrogen level is low, fill it to full capacity and wait for a minimum time of 6 hrs.

Increase the bias slowly stepwise (100 V in each step) or gradually to operating voltage of detector.

4.4.4 ENERGY CALIBRATION

Energy calibration is carried out using a solid or sealed liquid source of mixed radionuclides kept on the detector. The sources commonly used are ^{133}Ba, ^{137}Cs and ^{60}Co. Sometimes multiple gamma emitting standard source like ^{226}Ra is also used. The

gain of spectroscopy amplifier or built-in amplifier of analyser is adjusted to get required energy calibration of 1 keV/ch or 2 keV per channel. For example ^{137}Cs 662 keV gamma peak should fall on 331st channel if calibration of 2 keV/ch is required. The peak position can be seen by moving the cursor along the spectrum. Linearity of the system has to be checked by plotting a graph of energy against corresponding channel number with respective peaks of ^{133}Ba, ^{137}Cs and ^{60}Co. Fig.4.4 shows the energy calibration spectrum of Ge detector obtained with calibration factor of 2 keV/channel.

4.4.5 EFFICIENCY CALIBRATION

Determination of efficiency is essential for quantitative estimation of radionuclides in the environmental samples. Following points are to be remembered.

a) Sample to detector geometry

b) Calibration sources: As far as possible, standard source of the radionuclide to be estimated should be used. Alternatively efficiency v/s energy curve has to be drawn for each geometry and required efficiency can be noted from the graph.

c) Efficiency are expressed as radionuclide counting efficiency taking into account total disintegration rate or gamma energy efficiency by applying the gamma abundance factor (number of gammas per disintegration) of the source used. While making calculation, this point is to be taken care of.

The system's efficiency for a particular geometry and container used has to be determined. For example if 20 ml bottle of cylindrical geometry is used for sample counting, standard also has to be taken in 20 ml bottle of the same geometry. Care should be taken to keep the sample in the same configuration with respect to detector. As far as possible, standard calibration source should have same or similar physical properties as the sample. Certified reference standards are available from IAEA, IRC and other established suppliers. If solid standards are not available they can be prepared by spiking with known standard solution followed by drying and homogenisation .

EXPERIMENTAL

The standard solution of ^{137}Cs in 20 ml bottle or 5 ml vial is kept on Ge detector. Count for 300 secs. Intensify the area under the photo peak and take print out. Percentage efficiency can be calculated as follows.

$$E\,(\%) = N \text{ x } \frac{100}{dps} \text{ x } \frac{100}{A}$$

E = efficiency of the system for particular gamma energy.

N = net counts under the photo peak area after subtracting the background in cps.

dps = activity of standard (Bq).

A = Percent abundance of that particular energy out of total disintegration.

Similarly efficiencies can be calculated for different gamma energies and geometries using sources of ^{133}Ba, ^{60}Co, ^{134}Cs, ^{54}Mn, etc. A graph is drawn taking logarithm of energy (keV) in X-axis and logarithm of efficiency in Y-axis.

4.4.6 RESOLUTION

Resolution of the detector is its ability to distinguish between two gamma energies which are close to each other. It is quantified by specifying it as full width at half maximum (FWHM) for a particular gamma ray peak energy. By convention, HPGe detectors are usually characterised by the FWHM in keV at 1332 keV gamma of ^{60}Co. In a good HPGe system this is about 2 keV. Two gamma energies separated by less than two resolution widths (FWHM) are usually not resolved.

EXPERIMENTAL

Collect gamma spectrum of ^{60}Co by keeping a 5 ml vial source or solid disc source for adequate time to get well defined peaks. Take printout of 1173 and 1332 keV intensified peaks. Draw the spectrum on a linear or log linear graph.

Measure the width at half maximum and express in keV. FWHM can also be calculated by the formula given below.

$$FWHM \text{ (keV)} = \frac{Nr \text{ x } 159}{(X_2 - X_1)}$$

Nr - the width at half maximum in no. of channels

X_2 - Position of 1332 peak channel.

X_1 - Position of 1173 peak channel

159 keV is the difference between 1173 and 1132 keV gamma peaks of ^{60}Co.

4.5 IDENTIFICATION AND ESTIMATION OF GAMMA EMITTERS IN DIFFERENT SAMPLES

4.5.1 INTRODUCTION

Every gamma emitting nuclide has its characteristic gamma energy and decay scheme. Decay scheme of commonly observed fission and activation products are listed in Table 4.1. A complete list of commonly encountered gamma emitters is given in Nuclear Data sheets published by Academic Press, USA. While identifying multiple gamma emitters special care is needed. Complete knowledge of different peaks and their intensities are essential. While counting bulk environmental samples like soil and biological samples natural gamma emitters like ^{40}K and a host of peaks due to uranium and thorium daughter products are present.

4.5.2 IDENTIFICATION

Before identifying the gamma energies the following points may be kept in mind.

a) Background spectrum has to be stripped from sample + background spectrum before attempting the identification of nuclides.

b) Nature of sample counted and its history has to be considered. For example a waste sample of a BWR may have ^{60}Co in addition to ^{134}Cs and ^{137}Cs while a waste sample of FRP would invariably show gamma peaks due to ^{106}Ru, ^{144}Ce and ^{137}Cs. The same logic applies to samples collected near discharge zones.

c) Bulk environmental samples collected away from discharge zone of nuclear installations mainly show gamma peaks of natural background (^{40}K, U and Th series daughter products). Traces of fallout Cs-137 is also present.

d) Gamma peak at 511 keV comes from high energy gamma emitters > 2 MeV due to pair production and also due to annihilation of electron positron emitters. (e.g. ^{58}Co). For example while calculating the concentration of ^{106}Ru using 512

keV peak it has to be seen   that the second peak at 622 keV is also present with appropriate ratio of 512/622 keV peaks for ^{106}Ru.

4.5.3 ESTIMATION OF RADIONUCLIDE CONTENT

Selection of suitable geometry and counting duration is important for optimum utilization of the system. Counting time for process water, waste and contaminated samples could be in the range of 100 - 3000 secs. Background level samples should be counted preferably for 50,000 secs or more. The detector system has to be calibrated using standard solution/solid sources for different geometries as described earlier. Table-4.2 lists the typical % efficiency of HPGe detector of volume 50 cc mounted vertically on a cryostat.

4.5.4 SAMPLE ACTIVITY MEASUREMENT

a.   Prepare sample with appropriate geometry. Note the weight/volume of the sample.

b.   Take gamma spectra for preset duration depending on the nature and history of sample.

c.   From the spectrum identify the photo peaks of full energy and from that identify the nuclides.

d.   By taking area count rate of the full energy peak and using appropriate efficiency, calculate the quantity of radionuclide present in the sample in units of Bq/l or Bq/kg. Sample activity can be calculated as,

e.   Evaluate efficiency E of the relevant peak using similar sample. (volume/geometry/weight)

$$Q(Bq/kg \text{ or } Bq/l) = CPS \times \frac{100}{E} \times \frac{100}{A} \times \frac{1}{W \text{ or } V}$$

Q   = activity due to radionuclide

CPS   =   AREA COUNTS/TIME under photopeak after subtracting the background.

A   = % gamma abundance of radionuclide.

E   =   Counting efficiency in %

60

W = Weight of the sample in kg or V in litres.

4.5.5 DATA SHEET

i) Weight of the original sample taken W in kg or V in litres.

ii) Counting time = secs.

iii) From gamma spectra note down major peaks and the channel No. and enter data in the following table.

S.N	Peak Channel No.	Energy keV	Radio-nuclide	Area count rate (N)	Abundance (A%)	Efficiency% (E%)	Activity (Bq/kg) or Bq/l
1							
2							
3							
4							
5							
6							

N = Photo peak area / live time

TABLE - 4.1 GAMMA ENERGY FOR EVALUATION OF GAMMA EMMITING NATURALLY OCCURING RADIONUCLIDES

\

Energy keV	Radionuclide	Half-life d-days y-years	%Gamma Abundance
186.00	Ra-226	1600 y	46.0
300.08	Pb-212	10.64 h	3.34
295.17	Pb-214	26.8 m	19.2
583.17	Tl -208	3.05 m	86.0
609..32	Bi-214	19.1 m	46.1
911. 18	Ac-228	6.13 h	29.0
1460.80	K-40	1.28 E 9 y	10.7
1764.50	Bi-214	19.1 m	15.9

AP :

Activation product   FP: Fission product

N : Naturally occurring   A : Artificially produced

volume plastic bottle or Marinelli Beaker. If the radionuclides of interest are only I-131 and Cs-137, the acidified water with iodine and cesium carries is stirred with AMP and AgCl (2-5g). Allowed to settle. Supernates are decanted and residue is counted in HPGe detector with suitable geometry.

4.5.6 SOIL/SEDIMENT
Transfer homogenised powdered sediment/soil to 1 l Marinelli Beaker and count in HPGe for 10,000-20,000 secs duration.

4.5.7 MARINE/FRESH WATER ORGANISMS
Homogenised dried tissue samples (500-1000 g) are subjected to similar procedure as described for crop, vegetable etc.

4.5.8 MARINE/FRESH WATER ALGAE
Fresh sample is dried or ashed and counted in either in HPGe or NaI(Tl) detector.

4.6 ALPHA SPECTROMETRY

4.6.1 INTRODUCTION
Alpha spectrometry is used to identify and determine the concentration of various alpha emitting radionuclides such as ^{238}Pu, $^{239+240}$Pu, ^{241}Am, ^{242}Cm and ^{237}Np. Samples from various matrices are subjected to radiochemical separation of respective radionuclides and the separated sample is electrodeposited on a stainless steel planchet to count in alpha spectrometer.

4.6.2 INSTRUMENTATION
The alpha spectrometer system consists of a silicon surface barrier detector of suitable size (generally 450 mm^2 area, 100 μm depth) in a vacuum system, a bias unit, low voltage unit,   charge sensitive preamplifier, spectroscopy amplifier coupled to a multichannel analyser.   The system is calibrated with standards ^{239}Pu, ^{242}Pu and ^{241}Am sources at 0.01 mm Hg vacuum in the detector chamber.

4.6.3 ENERGY CALIBRATION
Electro plated sources of about 50 Bq concentration each of ^{239}Pu (5.155 MeV), ^{242}Pu (4.90 MeV) and ^{241}Am (5.486 MeV) either as single or mixed sources are used to carry out energy calibration. Amplifier gain and the conversion gain of multichannel analyser are adjusted such that an energy calibration of about 10 keV/channel is arrived. (Peak position of ^{239}Pu 515th or 516th channel). Linearity of the system is verified by counting the other sources under the same setup. A linear equation of energy versus channel number is established by using the three discrete alpha energies and the respective channel numbers.

4.6.4 EFFICIENCY CALIBRATION
Electro-plated sources of about 50 Bq concentrations each of ^{239}Pu, ^{242}Pu, ^{241}Am are prepared.   Each of them is counted for about 300 seconds in a well evacuated chamber. Vacuum for each standard should be same and must be less than 0.01 mm Hg. The distance between the sources and the detector should be fixed at about 2 mm. The efficiency of the spectrometer decreases rapidly with the increase in the distance between detector and source.

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$$S\% = \frac{Ar}{t} \times \frac{100}{Q} \times \frac{100}{I}$$

S% = Percent efficiency

Ar = Area under the peak (Background is negligible)

t   = Counting time in secs

Q   =   Source strength (Bq)

I   =   Percent abundance of alphas (No of alphas per 100 disintegrations)

Similar set up conditions must be used for the counting of electrodeposited sample of environmental matrices.

4.6.5 RESOLUTION

Energy resolution of a detector amplifier system is expressed as energy at full width half maximum (FWHM). An electroplated [241]Am source of about 50 Bq is positioned of in the surface barrier detector chamber. Spectrum is acquired till sufficient number of counts is accumulated under the photo peak. Number of channels at the half maximum counts is computed and expressed in keV after multiplying with appropriate energy calibration factor. As far as possible mono-energetic nuclide should be used. The energy resolution obtained from an alpha spectrometric system is mainly dependent on the detector, uniform thickness of source, amplifier and the analyser.

Though the detectors are quoted to have a resolution of about 20 keV, (FWHM) it is difficult to obtain the same in practice when different components are integrated in to an alpha spectrometric system. A resolution of about 50 keV or less is acceptable in the analysis of alpha emitters for the environmental samples. Details of calculation of resolution are same as that for gamma spectrometry (cf 4.6.9).

4.6.6 DETECTION

The range of alpha particles is only a few centimeters in air and much less in solids. Attenuation of energy causes deterioration in efficiency and resolution since alpha rays do not reach the detector. It is, therefore, necessary to have a thin source and to keep the source and detector in vacuum to obtain maximum energy resolution and high efficiency. In addition, the metal vacuum system serves as shielding against

background alpha particles and as an electric shield. The background of the detector amplifier system should not be more than 1 count per 10^4 seconds in the energy range of 0.5 to 10 MeV. The samples are normally counted for 5 X 10^3 seconds or longer depending upon the activity levels.

4.7 LIQUID SCINTILLATION ANALYSER (LSA)

The most widely used beta spectrometry is that of Liquid Scintillation Analysers (LSA) and the radionuclides estimated are ^{3}H, ^{14}C and ^{90}Sr by Cerenkov counting etc. The utilization of LSA for the purpose has been already explained in the earlier section.

5 ANALYTICAL METHODOLOGIES FOR WATER QUALITY PARAMETERS

5.1 ANALYTICAL METHODOLOGY

5.1.1 CHEMICAL PARAMETERS

5.1.1.1 ALKALINITY - Acid titration method

Alkalinity of water is the capacity of the water to accept proton. It may be quantitatively expressed as the capacity of an aqueous medium to react with hydrogen ions at pH 8.3 (phenolphthalein alkalinity) and then at pH 3.7 (total alkalinity or methyl orange alkalinity). This equation is as follows,

$$CO_3^{2-} + H^+ = HCO_3^- \quad (pH\ 8.3)$$

From pH 8.3 to 3.7, the following reaction may occur,

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$$
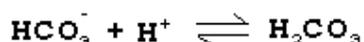
Reagents

Phenolphthalein indicator

0.5 g phenolphthalein dissolved in 100 ml of 60% ethyl alcohol

Methyl orange indicator

0.5 g methyl orange dissolved in 100ml 95% ethyl alcohol.

Sulphuric acid (0.02N)

0.2 N sulphuric acid was prepared by 5.5 ml of conc. H_2SO_4 diluted to 1 litre with distilled water. Then 10 times dilution was made for 0.02 N sulphuric acid preparation. The 0.02 N sulphuric acid was standardized with 0.02 N NaOH solution using phenolphthalein as indicator.

Method

➢ 25 ml of the water sample was taken into flask and add 2-3 drops of phenolphthalein. If pink colour is produced, it is titrated with standard 0.02 N sulphuric acid till pink colour disappears.

➢ Then 2 to 3 drops of methyl orange indicator was added to the above solution and titrated with standard 0.02 N sulphuric acid till the colour changes from yellow to pink colour. Record the volume of 0.02N sulphuric acid used for the titration.

Calculation and Result

$$\text{Total alkalinity (mg/l)} = \frac{T \times N \times E \times 1000}{V}$$
$$\text{(as } CaCO_3\text{)}$$

where,

          T - Titre value in ml

          N - Normality of standard sulphuric acid (0.02N)

          E - Equivalent weight of $CaCO_3$ (50)

          V - Volume of sample taken in ml.

The result is expressed in mg/l as $CaCO_3$.

5.1.1.2 TOTAL HARDNESS - EDTA titration method

EDTA titration method depends on ability of ethylene-di-amine tetra acetic acid (EDTA - $C_{10}H_{14}O_8N_2$) or its di sodium salt to form stable complexes with calcium and magnesium ions.

When the dye Eriochrome Black T (EBT - $C_{20}H_{13}N_3O_7S$) is added to solution containing calcium and magnesium ions at pH 10, a wine red complex is formed. This solution is treated with standard solution of di sodium salt of EDTA, which extracts calcium and magnesium from the dye complex and the dye is changed back to its original blue colour.

Reagents

Buffer solution

Dissolve 16.9 g of ammonium chloride (NH_4Cl) in 143 ml of conc. ammonium hydroxide (NH_4OH) and add 1.25 g of magnesium salt of EDTA and diluted to 250 ml with distilled water.

Store the solution in a polyethylene bottle tightly and store no longer than 1 month. During experiment, 10 ml of the solution made up to 100 ml with distilled water and check the pH value is 10 ± 0.1.

Eriochrome Black T (EBT) indicator

Grind 0.4 g of Eriochrome black T with 100 g NaCl (A.R).

Standard EDTA solution (0.01 M)

Dissolve 3.72 g EDTA dihydrate (which has been dried overnight in a sulphuric acid desiccator) in distilled water and dilute to 1 litre with distilled water.

Standard Calcium Carbonate solution (1 ml = 1mg CaCO$_3$)

Weigh 1 g CaCO$_3$ (dry AR grade) suspend it in distilled water and add Conc. HCl, drop wise slowly to dissolve the solid. Boil for few minutes, cool and add a few drops of methyl orange indicator and adjust to orange colour with 3 N NH$_4$OH. This solution is diluted to 1 litre with distilled water.

Method

> 0.01 M EDTA solution was standardized with standard calcium solution (1 ml EDTA solution = 1 mg calcium carbonate solution)

> 25mL of sample was taken in a conical flask and 1 ml of buffer was added to this solution.

> Then add approximately 100 mg of Eriochrome black T indicator and this solution titrated with standard 0.01 M EDTA solution till the colour changes from wine-red to blue.

Calculation and Result

$$\text{Total Hardness (mg/1)} = \frac{T \times E \times 1000}{V}$$
$$\text{[as CaCO}_3\text{]}$$

where,

T - Titre value in ml

E - Mass of CaCO$_3$ equivalent to EDTA solution (1 ml of EDTA = 1 mg CaCO$_3$)

V - Volume of sample taken in ml.

The result is expressed in mg/l as CaCO$_3$.

5.1.1.3 CALCIUM - EDTA titration method

In a solution containing both calcium and magnesium, calcium can be determined directly with EDTA. When the pH is made sufficiently high (12 to 13), magnesium is largely precipitated as the hydroxide and an indicator is used which combines only with calcium.

Reagents

Murexide (ammonium purpurate) indicator

Grind 0.2 g Murexide with 100g of NaCl.

NaOH solution (1 N)

40 g of NaOH is dissolved in 1 litre distilled water.

Standard EDTA solution (0.01 M)

As per total hardness estimation

Method

❖ 25 mL of the sample was taken in a conical flask and 2.0 mL of NaOH solution was added to this solution.

❖ Then add approximately 100 mg of Murexide in the solution and this solution was titrated with standard EDTA solution until the pink colour changes to dark purple.

Calculation

$$\text{Calcium(mg/l)} \atop [\text{as Ca}] = \frac{T \times E \times 1000}{V}$$

where,

T - Titre value in ml.

E - Mass in mg of calcium ions equivalent to 1 ml of EDTA solution

(1 ml EDTA = 0.4008 mg Ca)

V - Volume of sample taken

The result is expressed in mg/l as Ca.

5.1.1.4 MAGNESIUM - Calculation method through EDTA titration

When water sample containing both calcium and magnesium is titrated with EDTA at pH 10, using Eriochrome Black - T indicator which estimates calcium and magnesium. In a separate titration against EDTA at pH 12 to 13 range using Murexide indicator, calcium is selectively estimated. From these two values, magnesium concentration may be calculated.

Calculation and result

$$\text{Magnesium (mg/l)} = \frac{(TH-Ca) \times E \times 1000}{V}$$
$$\text{(as Mg)}$$

where,

    TH - Titre value for total hardness

    Ca - Titre value for Calcium

    E - Mass of magnesium equivalent to 1ml of EDTA (1 ml = 0.243 mg magnesium)

    V - Volume of sample in ml.

       The result is expressed in mg/l as Mg.

5.1.1.5 SODIUM AND POTASSIUM - Flame Photometric Method

The amount of sodium and potassium can be determined by Flame Emission spectroscopy (FES) at a wavelength of 589 nm for sodium and 766.5 nm for potassium. The sample is sprayed into a gas flame and excitation is carried out under carefully controlled and reproducible conditions. The desired spectral line is isolated by the use of interference filter or by a suitable slit arrangement and light, dispersing devices such as prisms or gratings. The intensity of light is measured by a phototube potentiometer or other appropriate circuit. The intensity of light at particular wavelength is approximately proportional to the concentration of the element.

Instrument

    ELICO Flame Photometer CL 361.

Reagents

Sodium standard solution (1000 ppm)

Dissolve 2.5422 g of AR grade of sodium chloride (previously dried at 140° for 1 hour) in little double distilled water and make up to 1000 ml in a volumetric flask (1 ml = 1.0 mg Na).

Potassium standard solution (1000 ppm)

Dissolve 1.90 g of AR grade of potassium chloride (previously dried at 140° for 1 hour) in little double distilled water and make up to 1000 ml in a volumetric flask (1 ml = 1.0 mg K).

Method

> ➢ Calibration curves for sodium and potassium were prepared by using standard solutions in the range of 0 to 100 ppm separately at a wavelength of 589 nm for sodium and 766.5 nm for potassium. Double distilled water was used as blank in every experiment.

> ➢ The sample is sprayed into a gas flame of flame photometer and determines the sodium and potassium separately.

> ➢ The results were obtained directly as concentrations of sodium and potassium present in the sample with the help of calibration curves.

> ➢ If the obtained result is higher than maximum limit of calibration curve, that sample was diluted with distilled water and again read.

Results

The results are expressed in mg/l as Na for Sodium and mg/l as K for potassium.

5.1.1.6 DISSOLVED OXYGEN - Winkler's method

When manganous sulfate is added to the sample containing alkaline potassium iodide, manganous hydroxide is formed, which is oxidized by the dissolved oxygen of the sample to basic manganic oxide. On addition of sulphuric acid, the basic manganic oxide liberates iodine equivalent to that of dissolved oxygen originally present in the sample. The liberated iodine is titrated with standard solution of sodium thiosulfate using starch as the indicator

Reagents

Manganous sulphate solution

Dissolve 100 g of manganous sulphate in 200 mL of previously boiled distilled water and filter the solution.

Alkaline potassium iodide solution

Weigh 50 g of potassium iodide and 100 g of potassium hydroxide and dissolve the chemicals in 200 mL of previously boiled and cooled distilled water.

Sodium thiosulphate solution (0.025 N)

Dissolve 3.95 g of sodium thiosulphate in previously boiled distilled water and make the volume up to 1 litre. The sodium thiosulphate solution is standardized with standard solution of potassium iodate (KIO_3) or potassium dichromate ($K_2Cr_2O_7$).

Starch indicator

Dissolve 1 g of starch in 100 mL of warm distilled water and add a few drops of toluene or formaldehyde as preservative

Concentrated sulphuric acid (Sp. Gr. 1.84)

Method

The water sample was filled in a glass stoppered BOD bottle avoiding any bubbling. No air should be trapped in bottle after the stopper in placed.

➤ 1 ml of each manganous sulphate and alkaline potassium iodide solutions were poured in this bottle using separate pipettes.

➤ A precipitate will appear. Place the stopper and shake the bottle thoroughly. The above steps were done in the time of sampling.

➤ After return to the lab, 2 ml of sulphuric acid was added and shake thoroughly to dissolve the precipitate.

➤ Gently 50 ml of solution was transferred to a conical flask and a few drops of starch indicator was added. Then it was titrated against sodium thiosulphate solution and the end point was noted when initial blue colour turned to colourless.

Calculation and Result

$$\text{Dissolved Oxygen (mg/L)} \text{ (as } O_2) = \frac{\text{Titrate value} \times N \times E \times 1000}{V_1 \{ (V_2 - V_3)/ V_2 \}}$$

where,

N = normality of sodium thiosulphate (0.025)

E = equivalent weight of oxygen (8)

V_1 = volume of fraction of the contents used for titration (mL).

V_2 = volume of sampling bottle after placing the stopper (mL).

V_3 = volume if manganous sulphate + potassium iodide solution added (mL)

The result is expressed in mg/l as O_2.

5.1.1.7 BIOCHEMICAL OXYGEN DEMAND (BOD) - Bio assay and Winkler's method

The Biological Oxygen Demand is based on mainly bio-assay procedure which measures the dissolved oxygen consumed by microorganisms while assimilating and oxidizing the organic matter under aerobic condition.

Reagents

Phosphate buffer solution

Dissolve 8.5g potassium dihydrogen phosphate (KH_2PO_4), 21.75 g dipotassium hydrogen phosphate (K_2HPO_4), 33.4 g disodium hydrogen phosphate ($Na_2HPO_4.7H_2O$) and 1.7 g of NH_4Cl in about 500 ml distilled water and dilute to 1 litre. pH of the solution should be around 7.2 without any further adjustment.

Magnesium sulphate solution

Dissolve 22.5g of magnesium sulphate ($MgSO_4. 7H_2O$) in distilled water and dilute to 1 litre.

Calcium chloride solution

Dissolve 27.5g of anhydrous calcium chloride in distilled water and dilute to 1 litre.

Ferric chloride solution

Dissolve 0.25g of ferric chloride hexahydrate in 1 L distilled water.

All reagents used in Dissolved Oxygen

Preparation of dilution water

Aerate the required amount of distilled water in a container by bubbling compressed air for 8-12 hours to attain dissolved oxygen saturation. Let it stabilize for 4 hours at room temperature.

At the time of use, 1 ml each of calcium chloride, magnesium sulfate solution, ferric chloride solution, phosphate buffer solution is added to one litre of dilution water.

If seeding is needed, 2 to 5 ml of treated sewage (or domestic sewage) is added to 1 litre of dilution water.

Method

If dilution is not required, following procedure is carried out,

- Each 1 mL of calcium chloride, magnesium sulfate solution, ferric chloride solution, phosphate buffer solution was added to one litre of the water sample. Two sets of BOD bottles were filled with this water sample and stopper the bottle immediately.
- Determine the dissolved oxygen content (DO_0) in one set immediately following the Winkler's method of dissolved oxygen.
- Incubate the other set in BOD incubator for 5 days at 20° C.
- Take out the bottles after 5 days and determine immediately their dissolved oxygen content (DO_5)

If dilution is required, following procedure is carried out,

Requisite quantity of water sample was taken in 1 litre of volumetric flask and it was diluted to 1 litre with dilution water by siphoning.

- Two sets of BOD bottles were filled with the diluted sample and stopper the bottle immediately.
- Determine the dissolved oxygen content (DO_0) in one set immediately following the Winkler's method of dissolved oxygen.
- Incubate the other set in BOD incubator for 5 days at 20° C.
- Take out the bottles after 5 days and determine immediately their dissolved oxygen content (DO_5)

Calculation and Result

(i) When sample is undiluted,

Biological Oxygen Demand (mg/L) = DO_0 - DO_5

(as O_2)

where,

DO_0 is the initial dissolved oxygen content in mg/l

DO_5 is the dissolved oxygen after 5 days incubation.

(ii) When sample is diluted,

$$\text{Biological Oxygen Demand (mg/L)} = \frac{(DO_0 - DO_5) \times 100}{P}$$

(as O_2)

Where,

DO_0 - initial dissolved oxygen content in mg/l

DO_5 - dissolved oxygen after 5 days incubation

P - percentage dilution of water sample.

The result is expressed in mg/l as O_2.

5.1.1.8 CHEMICAL OXYGEN DEMAND (COD) - Reflux titration method

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. A sample is refluxed in strong acid solution with a known excess of potassium dichromate. After digestion, the remaining unreduced potassium dichromate is titrated with ferrous ammonia sulfate to determine the amount of potassium dichromate consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent.

Reagents

Potassium dichromate solution (0.25N)

Dissolve 12.259 g of potassium dichromate, previously dried at 103^0c in distilled water and dilute to one litre

Dry powder of silver sulphate

Dry powder of mercuric sulphate

Conc.H_2SO_4 (Sp. Gr. 1.84)

Ferroin indicator solution

Standard ferrous ammonium sulphate solution (0.25N)

Dissolve 98 g of ferrous ammonium sulphate in distilled water, add 20mL of sulphuric acid, cool and dilute to 1L by further adding distilled water.

To standardize this solution, dilute 25mL of potassium dichromate solution to about 240 mL with distilled water, add 20mL of sulphuric acid, and cool it. Add 5-6 drops of ferroin indicator solution and titrate against ferrous ammonium sulphate solution. The colour changes from blue green to reddish blue at end point. The exact normality of FAS is calculated as,

$$\text{Normality of FAS} = \frac{\text{Volume of } k_2Cr_2 O_7 \text{ (mL) x O.25}}{\text{Volume of FAS (mL)}}$$

Method

➢ 20 ml of sample was taken in the flask of reflux unit and add 10mL of potassium dichromate solution, a pinch of each silver sulphate and mercuric sulphate and 30mL of sulphuric acid were added.

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- The contents were refluxed for 2 hrs.
- The flask was cooled, detach from unit and content dilute to about 150mL by adding distilled water.
- 2-3 drops of ferroin indicator was added to the solution and titrated against ferrous ammonium sulphate solution.
- The end point was noted when blue green colour of contents changed to reddish blue.
- Simultaneously blank using distilled water was run in a similar manner.

Calculation and Result

$$\text{Chemical Oxygen Demand (mg/l) (as O}_2\text{)} = \frac{(B-T) \times N \times E \times 1000}{\text{Volume of sample (mL)}}$$

where,

T= volume of titrant (FAS) used against sample (mL).

B= volume of titrant used against blank (mL)

N= normality of Ferrous Ammoniam Sulphate

E = equivalent weight of oxygen (8)

The result is expressed in mg/l as O_2.

5.1.1.9 CHLORIDE - Argentometric method

Silver Nitrate reacts with chloride in neutral or alkaline solution to form silver chloride. Potassium chromate is used as indicator in the silver nitrate titration of chloride estimation. Potassium chromate also reacts with silver nitrate to form red silver chromate. However, this potassium chromate reaction is less favourable than the chloride reaction. So potassium chromate only reacts with silver nitrate in the absence of free chloride ions in the water sample.

When no free chloride is left in the solution at the end point, addition of a drop of silver nitrate titrant results in the formation of silver chromate producing a pink end point.

Reagents

Silver nitrate (0.02N)

3.40g of Silver nitrate is dissolved in double distilled water and make upto 1 litre. The 0.02 N silver nitrate solution was standardized with 0.02 N sodium chloride solution.

Potassium chromate indicator

5% aqueous solution of pure K_2CrO_4

Method

➤ 5 ml of sample was taken and diluted to 25 ml with distilled water. Then 5 to 6 drops of K_2CrO_4 was added to this sample.

➤ This solution was titrated with standard $AgNO_3$ solution till the first brick red tinge appears.

Calculations

$$\text{Chloride (mg/l)} \ (\text{as Cl}) = \frac{T \times N \times E \times 1000}{V}$$

where,

T - titrate value

N - normality of silver nitrate (0.02)

E - equivalent weight of chloride (35.45)

V - volume of sample taken in ml.

The result is expressed in mg/l as Cl.

5.1.1.10 FLUORIDE - SPADNS Spectrophotometric method

The SPADNS spectrophotometric method is based on the reaction between fluoride and a zirconium-dye lake (SPADNS dye). Fluoride reacts with the dye lake in the presence zirconyl acid, dissociating a portion of it into a colourless complex anion and the dye. As the amount of fluoride increases, the colour produced by the dye progressively lighter.

Reagents

SPADNS solution

Dissolve 958 mg of SPADNS [Sodium 2-(Parasulphophenyl Azo)-1, 8-Dihydroxy-3, 6-Naphthalene di Sulphonate trisodium salt] in distilled water and dilute to 500 ml.

Zirconyl - acid reagent

Dissolve 133 mg zirconyl chloride octahydrate in 25 ml distilled water. Add 350 ml of Conc. HCl and dilute to 500 ml with distilled water.

Acid zirconyl - SPADNS reagent

Mix equal volumes of SPADNS solution and zirconyl acid reagent.

Standard fluoride solutions

Dissolve 221 mg anhydrous sodium fluoride in distilled water and dilute to 1 litre (1 ml = 100 μg of F⁻).

From the above stock solution, prepare standard solutions in the range of 0.2 to 1.4 mg/l of F.

Method

➢ Prepare a calibration curve in the range of 0.0 to 1.4 mg/l of F at the interval of 0.2, by using the following same method. Distilled water used as blank.

➢ 50 ml of the sample was taken in a conical flask.

➢ 10 ml of acid zirconyl-SPDANS reagent was added to the sample and mix well.

➢ After 1 hour, the optical density of the solution was read on spectrophotometer at 520 nm.

➢ If the concentration of sample is higher than upper range of calibration curve, sample is diluted with distilled water.

Result

The result is expressed in mg/l as F.

5.1.1.11 PHOSPHATE - Stannous chloride Spectrophotometric method

Ammonium molybdate reacts with phosphate present in water to form molybdophosphoric acid at low pH which is reduced to a blue colored complex, "molybdenum blue" by the addition of stannous chloride.

Reagents

Ammonium molybdate solution

(a) Dissolve 25.0g of ammonium molybdate in 175mL of distilled water

(b) Add 280 ml of Conc. H_2SO_4 to 400mL of distilled water and cool

Mix the two solutions (a) and (b) and make up the volume to 1 litre with distilled water.

Stannous chloride solution

Dissolve 2.5g of stannous chloride in 100mL glycerol by heating on a water bath.

Standard phosphate solution

Dissolve 0.22 g of pre-dried anhydrous potassium hydrogen phosphate (K_2HP0_4) in distilled water and make up the volume to 1 litre (1 ml = 50 µg PO_4-P).

From the above stock solution, prepare standard solutions in the range of 20 to 200 µg/l of PO_4-P.

Method

➢ Prepare a calibration curve in the range of 0.0 to 200µg/l of PO_4 –P at the interval of 20, by using the following method. Distilled water used as blank.

➢ 50 ml of filtered water sample was taken in a conical flask.

➢ If the sample in having colour and colloidal impurities, remove them by adding a spoonful of activated charcoal and filter it. If colour is not removed, 2 ml of perchloric acid was added after evaporation of 50 ml of sample to dryness and made up to 50 ml with distilled water.

➢ 2 ml of ammonium molybdate solution and 5 drops of stannous chloride reagent was added to this sample.

➢ A blue colour will appear in presence of phosphate.

➢ After 5 minutes but before 12 min., the optical density of the solution was read at 690 nm on a spectrophotometer.

➢ If the concentration of sample is higher than upper range of calibration curve, sample is diluted with distilled water.

The result is expressed in µg/l as PO_4 –P.

5.1.1.12 SULPHATE - Turbidity Spectrophotometric Method

Sulphate ion is precipitated in the form of Barium sulphate by adding Barium chloride in hydrochloric acid medium. The concentration of sulphate can be determined from the absorbance of the light by Barium sulphate and then comparing it with a standard curve.

Regents

Conditioning reagent

Mix 75 g of NaCl, 30 ml Conc. HCl (Sp. Gr. 1.18), 100 ml 95 % ethyl alcohol in 300 ml of distilled water. Add 50 ml glycerol to this solution and mix thoroughly.

Hydrochloric acid solution (1 + 1)

Standard Sulphate solution

Dissolve 1.479 g of anhydrous Na_2SO_4 in distilled water to make 1 litre of solution. (1 ml = 1 mg SO_4)

From the above stock solution, prepare standard solutions in the range of 5 to 40 mg/l of SO_4.

Method

➢ Prepare a calibration curve in the range of 0.00 to 40.0 mg /l of SO_4 at the interval of 5 mg/l, by using the following method. Distilled water used as blank.

➢ 20 ml of sample was taken in a conical flask and add 1 ml of conditioning reagent

➢ Stir the solution on a magnetic stirrer and during stirring add a spoonful of $BaCl_2$ crystals. Stir only 1 minute after addition of $BaCl_2$.

➢ The optical density of the solution was read on a spectrophotometer at 420 nm after 4 minutes and find out the concentration of sulphate from the calibration curve.

➢ If the concentration of sample is higher than upper range of calibration curve, sample is diluted with distilled water.

Result

The result is expressed in mg/l as SO_4.

5.1.1.13 NITRATE - Brucine Sulphate Spectrophotometric method

Nitrate reacts with burcine in strong sulphuric acid solution to form a yellow color which is measured spectrophotometrically at 410 nm

Reagents

Nitrate standard solution

Dissolve 0.722 g of potassium nitrate (KNO_3) in 1 litre of distilled water (1 ml = 0.1 mg NO_3-N).From the above stock solution, prepare standard solutions in the range of 0.1 to 1 mg/l of NO_3-N.

Brucine-sulphanilic acid solution

Dissolve 1g brucine sulphate and 100 mg sulphanilic acid in 70 mL hot distilled water. Add 3mL. Conc. HCl, cool and dilute to 100 mL with distilled water

Sulfuric acid solution

Add carefully 500 mL Conc. H_2SO_4 to 75mL distilled water and cool to room temperature.

Method

➢ Prepare a calibration curve in the range of 0.00 to 1.0 mg /l of NO_3-N at the interval of 0.2 mg/l, by using the following method. Distilled water used as blank.

➢ 5 ml of sample was taken in a test tube and 1 ml brucine-sulphanilic acid solution was added to the sample.

➢ 10 ml sulfuric acid solution was placed in 50 ml beaker.

➢ Sample with brucine-sulphanilic acid solution was transfer to the 50 ml beaker containing sulfuric acid solution and mix well.

➢ Keep the beakers in dark for 10+1 minutes.

➢ While the colour is developing, 10 ml distilled water was added to this solution (but not before 10 minutes).

➢ Allow to cool in the dark for another 20-30 minutes.

➢ The optical density of the solution was read on spectrophotometer at a wavelength of 410 nm and find out the concentration of nitrate nitrogen from the calibration curve.

➢ If the concentration of sample is higher than upper range of calibration curve, sample is diluted with distilled water.

The result is expressed in mg/l as NO_3-N.

5.1.1.14 NITRITE - Diazotization Spectrophotometric method

Sulphanilic acid is diazotised by nitrite and the diazo compound is coupled with α - naphthylamine hydrochloride to form a reddish purple azo dye at a pH of 2.0 – 2.5.

Reagents

EDTA solution

Dissolve 500 mg disodium ethylene diamine tetra acetate dihydrate in distilled water and dilute to 100 ml.

Sulfanilic acid solution

Dissolve completely 600 mg of sulfanilic acid in 70 ml hot distilled water, cool and add 20 mL Conc. HCl dilute to 100 ml with distilled water.

α - Napthylamine hydrochloride solution

To 50 mL distilled water in a beaker, add 1 ml of Conc. HCl. Dissolve it in 600 mg of $\propto$ naphthylamine hydrochloride and dilute to 100 ml with distilled water.

Sodium acetate buffer solution, 2M

Dissolve 16.4 g sodium acetate or 27.2 g sodium acetate trihydrate in distilled water and dilute to 100 ml.

Nitrite standard solution

Dissolve exactly 493 mg sodium nitrite in distilled water and make up to 1000 ml in a volumetric flask (1 ml = 100 μg of NO_2-N).

From the above stock solution, prepare standard solutions in the range of 5 to 50 μg/l of NO_2-N.

Method

➢ Prepare a calibration curve in the range of 0.00 to 50.0 μg/l of NO_2-N at the interval of 5 μg/l, by using the following method. Distilled water used as blank.

➢ 50 ml of the sample was transferred into a Nessler's tube. 1 ml of EDTA solution was added to this solution and stir well.

➢ Then add 1.0 ml sulfanilic acid to the above solution and mix thoroughly. After 10 minutes, each of 1.0 ml $\propto$ napthylamine hydrochloride solution and sodium acetate buffer solution were added to this solution and mixed thoroughly.

➢ After 10 minutes, the optical density of the solution was read by spectrophotometer at 520 nm and the concentration of nitrite nitrogen found out from the calibration curve

❖ If the concentration of sample is higher than upper range of calibration curve, the sample is diluted with distilled water. The result is expressed in μg/l as NO_2-N.

5.1.1.15 SILICA - Molypdosilicate Spectrophotometric method

Ammonium molybdate at pH 1.2 reacts with silica and any phosphate present in the water sample to produce heteropolyacids. Oxalic acid is added to destroy the molybdophosphoric acid but not the molybdosilicic acid.

Reagents

Hydrochloric acid (1+ 1)

Ammonium molybdate solution (10%)

Dissolve 20g of ammonium molybdate in distilled water and make up the volume to 200mL. Adjust the pH between 7 and 8 by adding Ammonium hydroxide. Keep the solution in a polyethylene bottle.

Oxalic acid solution (10%)

Dissolve 20g of oxalic acid in distilled water and make up to 200mL

Standard silica solution

Dissolve 4.73 g of sodium meta silicate nanohydrate in distilled water and dilute to 1 litre with distilled water (1 ml = 1 mg SiO_2).

From the above stock solution, prepare standard solutions in the range of 2 to 10 mg/l of SiO_2.

Method

➢ Prepare a calibration curve in the range of 0.00 to 50.0 μg/l of NO_2-N at the interval of 5 μg/l, by using the following method. Distilled water used as blank.

➢ 50 ml of the water sample was taken in a conical flask and 1 ml of Hydrochloric acid and 2 ml of Ammonium molybdate solution were added to the sample.

➢ After 10 minutes, 1.5 ml of oxalic acid solution was added to this above solution.

➢ Mix thoroughly and the optical density of the solution was read on Spectrophotometer at 410mn and the concentration of silicate found out from the calibration curve.

➢ If the concentration of sample is higher than upper range of calibration curve, the sample is diluted with distilled water.

Result

The result is expressed in mg/l as SiO_2.

5.1.1.16 AMMONIA - Kjeldahl titration method

The sample is buffered at p H 9.5 with a borate buffer to decrease hydrolysis of cyanates of organic nitrogen compounds. It is distilled and absorbed into a solution of boric acid and ammonia is determined with standard mineral acid.

Reagents

Hydrochloric acid (0.01N)

Boric acid cum indicator solution

Dissolve 4g of boric acid in 100mL of warm distilled water. Prepare 0.5% bromocresol green solution and 0.1% methyl red solution in ethyl alcohol. Mix bromocresol green and methyl red solution in the ratio of 2:1 to make a mixed indicator. Add 5 ml of this mixed indicator to 100mL of boric acid solution. If the colour of solution becomes blue add 0.01N Hydrochloric acid until it turns faint pink to brown.

Borate buffer solution

Add 88 ml of 0.1 N of sodium hydroxide to 500 ml of 0.025 M sodium tetra borate solution and dilute to 1 litre with distilled water.

Sodium hydroxide solution (6 N)

Method

➢ 250 ml of sample was taken in a Kjeldahl flask. 15 ml borate buffer was added followed by 6 N sodium hydroxide until pH 9.5 was reached.

➢ 25mL of boric acid solution containing 2-3 drops of mixed indicator in a conical flask was placed below the condenser so that the tip of out let of the condenser is dipped in contents of conical flask.

➢ The kjeldhal flask containing solution was heated and continued the distillation until about 200 ml of distillate was collected in the conical flask.

➢ The conical flask having distillate was removed after distillation, which turns blue for dissolution of ammonia.

➢ The distillate was titrated against 0.01N Hydrochloric acid until blue colour changes to pink.

➢ A blank using distilled water was run in a similar way.

Calculation

$$\text{Total Organic Nitrogen (mg/L)} = \frac{(T-B) \times N \times E \times 1000}{\text{Volume of sample}}$$
$$\text{(as NH}_4\text{-N)}$$

Where,

> T - volume of titrant (HCl) used against sample (ml).
>
> B - volume of titrant (HCl) used against blank (ml).
>
> N - normality of HCl (0.01).
>
> E - equivalent weight of nitrogen (14).

The result is expressed in mg/l as NH_4-N

5.1.1.17 TOTAL ORGANIC NITROGEN - Kjeldahl titration method

In the presence of sulphuric acid, potassium sulfate and mercuric sulfate catalyst, amino nitrogen of many organic materials is converted to ammonium sulphate. Free ammonia and ammonium nitrogen are also converted to ammonium sulphate. For this purpose, free ammonia is removed from sample before digestion. During sample digestion, a mercury ammonium complex is formed and then decomposed by sodium thiosulphate. After decomposition, the ammonia is distilled from an alkaline medium and absorbed in boric acid. The ammonia is determined by titrated with standard mineral acid.

Apparatus

Micro-Kjeldahl apparatus

Reagents

Mercuric sulphate solution

8g of mercuric oxide is dissolved in 100 ml of 6 N sulphuric acid.

Digestion mixture

Dissolve 134g of potassium sulphate in 650 mL of distilled water and 200 ml of Conc. H_2SO_4. 25 ml mercuric sulphate solution is added to this solution with stirring. Then dilute to 1 litre with distilled water. Keep at a temperature close to 20° C to prevent crystallization.

Hypo solution

Dissolve 500 g of sodium hydroxide and 25 g of sodium thiosulphate pentahydrate in distilled water and dilute to 1 litre with distilled water.

Borate buffer solution

Add 88 ml of 0.1 N of sodium hydroxide to 500 ml of 0.025 M sodium tetra borate solution and dilute to 1 litre with distilled water.

Boric acid cum indicator solution

Dissolve 4g of boric acid in 100mL of warm distilled water. Prepare 0.5% bromocresol green solution and 0.1% methyl red solution in ethyl alcohol. Mix bromocreol green and methyl red solution in the ratio of 2:1 to make a mixed indicator. Add 5 mL of this mixed indicator to 100mL of boric acid solution. If the colour of solution becomes blue add 0.01N Hydrochloric acid until it turns faint pink to brown.

Hydrochloric acid (0.01 N)

Method

- ➤ 250 ml of sample was taken in a Kjeldahl flask. 15 ml borate buffer was added followed by 6N sodium hydroxide until pH 9.5 was reached. A few glass beads were added, boiling off and water sample was reduced to 100 ml.

- ➤ After cooling, 25 ml of digestion mixture was added carefully to the boiled solution until the volume is greatly reduced under a hood. During boiling, copious white fumes are observed and digestion continued for additional 15 min.

- ➤ After digestion, contents were cooled, then diluted to 200 ml with distilled water and mixed well. Then carefully 25 ml hypo solution was added to form an alkaline layer at flask bottom and flask connected to steam out distillation apparatus. (A black precipitate of mercuric sulphide will form in flask and pH should exceed 11).

- ➤ 25 ml of boric acid solution containing 2-3 drops of mixed indicator in a conical flask was placed below the condenser so that the tip of out let of the condenser is dipped in contents of conical flask.

- ➤ During distillation, 100 ml of distillate was collected in conical flask containing boric acid and mixed indicator.

- ➤ The distillate was titrated against Hydrochloric acid until blue colour changed to pink.

- ➤ Blank using distilled water was run in a similar way.

Calculation

$$\text{Total Organic Nitrogen (mg/L)} = \frac{(T-B) \times N \times E \times 1000}{\text{Volume of sample}}$$
$$\text{(as } NH_4\text{-N)}$$

Where,

        T - Volume of titrant (HCl) used against sample (ml).

        B - Volume of titrant (HCl) used against blank (ml).

        N - Normality of HCl (0.01).

        E - Equivalent weight of nitrogen (14).

The result is expressed in mg/l as NH_4-N

5.1.2 TRACE ELEMENTAL ANALYSIS - ATOMIC ABSORPTION METHOD

For estimation of Cadmium, Chromium, Cobalt, Copper, Iron, Lead, Manganese, Nickel, Strontium and Lead

The atomic absorption spectrometry is most common method for examination of a large number of inorganic and organic substances. In this technique, the sample is aspirated into a hot flame to convert the element to its atomic vapour. However in this case the absorption of specific radiation by the atoms is measured rather than the emission spectra. After atomization of the element in the flame, most of the atoms remain in their ground state. Majority of them can be raised to the excited state, if they are given some specific radiation. The specific radiation which they would otherwise emit while coming to ground state from their excited state. Such radiation is possible to obtain from a hollow cathode lamp made up of the same element. The absorption of this radiation follows Beer's law as applicable to the absorption spectrometry. The concentration of the element can be determined by using a calibration curve.

Instrument

Atomic Absorption Spectrophotometer

Method

Pretreatment of water sample

- ➢ The sample was filtered and acidified with Conc. HNO_3 to a pH less than 2 immediately after collection of sample.
- ➢ 1.5 litre of filtered sample was taken in a beaker and 5 ml of Conc. HNO_3 was added.
- ➢ The sample was evaporated to dryness on a hot plate preventing boiling.
- ➢ After cooling, another 5 ml of the Conc. HNO_3 was added. Continued heating, by adding some additional HNO_3 until light coloured residue formed.
- ➢ The residue was dissolved by adding 0.5 N HCl. The wall of the beaker was washed with 0.5 N HCl and the contents were filtered.

➢ The filtered content was made up to 50 ml with 0.5 N HCl.

After pretreatment of the water sample, the sample was aspirated into the flame for estimation of elements as per the Instrument instruction manual.

5.1.3 MICROBIOLOGICAL EXAMINATION OF WATER

1. Examination of Total Coli Forms - Most Probable Number Method (MPN)

Three basic tests are involved in the examination of coli forms in the water.

i)   Presumptive test

ii) Confirmative test

iii) Completed test

They detect the presence of coli form bacteria, the gram negative, non spore forming bacilli that ferment lactose with the production of acid and gas that is detectable following a 24-hour incubation period of 35° C.

i) The Presumptive Test

The presumptive test is specific for detection of coli form bacteria. Measured aliquots of the water to be tested are added to a lactose fermentation broth containing an inverted gas vial. Because these bacteria are capable of using lactose as a carbon source (the other enteric organisms are not) their detection is facilitated by the medium also contains a surface tension depressant, bile salt used to suppress the growth of organisms other than coli form bacteria

Medium

Lauryl Tryptose broth (LTB)

Method

➢ Three tubes of double strength Lauryl Tryptose broth and six tubes of single strength Lauryl Tryptose broth was prepared and marked each tube according to the amount of water that is to be dispersed to it (10ml, 1.0ml and 0.1ml).

➢ Durham's tube is inversely positioned in each of the broth containing tubes which is completely filled with broth.

➢ After sterilization, 10mL of water sample to each of the double Strength LT broth, 1ml of water sample to three tubes of single strength LT broth and 0.1 ml of water sample to three tubes of single strength LT broth were transferred in a sterile condition.

➢ The tubes were incubated at 35° C for 24 hr.

Observation

After 24 hrs of incubation, the tubes were observed. If 10% or more of gas appears in a tube, it is considered as positive. If there is no gas in a tube after 48 hours which is considered as negative.

ii) The confirmed test

The Confirmed test requires that selective and differential media such as endo agar be streaked from a positive LT broth tube obtained from the presumptive test. Endo agar is a nutrient medium containing the dye fuchsin, which is present in the decolorized state. In the presence of acid produced by the coliform bacteria, fuchsin forms a dark pink complex that turns the *E. coli* colonies and the surrounding medium pink.

Method

> Select a positive LT broth from the presumptive test and streak on to a plate of endo agar.

> Incubate the plates for 24 hr at 35°C.

Observation

After 24 hrs incubation, observe the plates for typical dark pink colour coliform colonies on the plates.

iii) The Completed Test

The completed test is the final analysis of the water sample. It is used to examine the coliform colonies that appeared on endo agar plates used in the confirmed test. An isolated colony is picked from the confirmatory test plate and inoculated into a tube of LT broth and streaked on a nutrient agar slant to perform a Gram stain. Following inoculation and incubation, tubes showing acid and gas in the LT broth and the presence of gram negative bacilli on microscopic examination are further confirmation of the presence of E. coli, and they are indicative of a positive completed test.

Calculation of Most Probable Numbers

The calculation of MPN of coli forms is done by combination of positive and negative results in the multiple tube tests. The values can be calculated for any of the combinations given in table (A).

2. Examination of Faecal Coliforms - Most Probable Number method

Since the coliforms in water may be derived from the sources other than the faecal, it is desirable to carry out a separate faecal coliform test for the sample where a doubt about the pollution of human origin arises. A faecal coliform is a facultative anaerobe which ferments lactose to produce gas and is a gram negative, non- spore forming rod. The major species in faecal coliform group is *E. coli.* Presence of this species regarded as an indication of faecal pollution and possibility of enteric pathogens.

Method

Presumptive test

The presumptive test is same as for total coliforms.

Confirmed test

➢ Transfer a loop full of culture from the positive Lauryl- Tryptose broth tubes to EC broth.

➢ Incubate the tubes at 35° C for 48hrs.

➢ Examine the tubes for the presence of gas in the Durham tube. Formation of gas in the Durham tube with in 4 to 8 hours constitute a positive confirmed test.

Completed test

➢ From the positive EC broth tubes, inoculate a loop full of culture on to endo agar plates.

➢ Incubate the plates at 35° C for 48hrs following incubation, examine the plates for results.

A positive test shows completely dark pink colonies and the surrounding medium is pink in colour.

Calculation of Most Probable Numbers

The calculation of MPN of coliforms is done by combination of positive and negative results in the multiple tube tests. The values can be calculated for any of the combinations given in table (A).

Table (A). MPN index and 95 % confidence limits for various combinations of positive tubes in a 3 tube dilution series using inoculum quantities of 10, 1 and 0.1 ml

Combination of Positive tubes	MPN index per 100 ml	95 % confidence limits	
		Lower	Upper
0-0-0	< 3.00	------	9.50
0-0-1	3.00	0.15	9.60
0-1-0	3.00	0.15	11.00
0-1-1	6.10	1.20	18.00
0-2-0	6.20	1.20	18.00
0-3-0	9.40	3.60	38.00
1-0-0	3.60	0.17	18.00
1-0-1	7.20	1.30	18.00
1-0-2	11.00	3.60	38.00
1-1-0	7.40	1.30	20.00
1-1-1	11.00	3.60	38.00
1-2-0	11.00	3.60	42.00
1-2-1	15.00	4.50	42.00
1-3-0	16.00	4.50	42.00
2-0-0	9.20	1.40	38.00
2-0-1	14.00	3.60	42.00
2-0-2	2.00	4.50	42.00
2-1-0	15.00	3.70	42.00
2-1-1	20.00	4.50	42.00
2-1-2	27.00	8.70	94.00
2-2-0	21.00	4.50	42.00
2-2-1	28.00	8.70	94.00
2-2-2	35.00	8.70	94.00
2-3-0	29.00	8.70	94.00
2-3-1	36.00	8.70	94.00
3-0-0	23.00	4.60	94.00
3-0-1	38.00	8.70	110.00
3-0-2	64.00	17.00	180.00

3-1-0	43.00	9.00	180.00
3-1-1	75.00	17.00	200.00
3-1-2	120.00	37.00	420.00
3-1-3	160.00	40.00	420.00
3-2-0	93.00	18.00	420.00
3-2-1	150.00	37.00	420.00
3-2-2	210.00	40.00	430.00
3-2-3	290.00	90.00	1000.00
3-3-0	240.00	42.00	1000.00
3-3-1	460.00	90.00	2000.00
3-3-2	1100.00	180.00	4100.00
3-3-3	> 1100.00	420.00	-----

3. Enumeration of *E. coli* - Standard Plate Count Technique

  ➢ The suitable aliquot of water sample is inoculated in selective agar of endo agar by pour plate method.

  ➢ The *E. coli* colonies appear dark pink in colour and surrounding of medium is pink. These colonies are counted under colony counter.

  ➢ If too numerable numbers of colonies appear in the plate, dilute the water sample and inoculated in endo agar plate, again counted and apply dilution factor.

4. Examination of *Salmonella sp* and *Shigella sp* - Standard Plate Count Technique

  ➢ The suitable aliquot of water sample is inoculated in selective agar of Salmonella Shigella (SS) agar by pour plate method.

  ➢ The *Salmonella sp* colonies appear in black colour. These colonies are counted under colony counter.

  ➢ The *Shigella sp* colonies appear in media colour of yellowish white. These colonies counted under colony counter.

  ➢ If too numerable numbers of colonies appear in the plate, dilute the water sample and inoculated in endo agar plate, again counted and apply dilution factor.

6) DETAILED PROCEDURES FOR THE DETERMINATION OF SO$_2$, NO$_2$ AND PARTICULATE MATTER CONCENTRATIONS IN AIR

6.1 DETERMINATION OF NITROGEN DIOXIDE IN THE ATMOSPHERE

(Jacob and Hochheiser modified method)

AIM

Determination of nitrogen dioxide in the atmospheric air by Jacob and Hochheiser modified method.

6.1.1 PRINCIPLE

Ambient Nitrogen dioxide is collected by bubbling air through a solution of sodium hydroxide and sodium arsenite. The concentration of nitrite ion produced during the sampling is determined colorimetrically by reacting the nitrite ion with Phosphoric acid, Sulphanilamide and N - (1 Naphthyl) – ethylenediamine di-hydrochloride (NEDA) and measuring the absorbance of the highly coloured azo dye at 540 nm.

6.1.2 INTERFERENCES

Nitric oxide (NO) is a positive interferent and carbon dioxide is a negative interferent. The average error resulting from normal ambient concentrations of NO and CO_2 is small for most monitoring situations and does not necessitate applying a correction to measurements obtained with the method. Potential interference from Sulphur dioxide is eliminated by converting SO_2 to sulphate with hydrogen peroxide during the analysis.

6.1.3 ABSORBING REAGENTS

Dissolve 4 g of Sodium hydroxide in distilled water. Add 1 g of Sodium arsenite and dilute to 1000 ml with distilled water.

6.1.4 ANALYSIS

Sulfanilamide solution

Dissolve 20 g of Sulphanilamide in 700 ml of distilled water. Add 50 ml of 85% phosphoric acid and dilute to 1000 ml. This solution is stable for one month, if refrigerated.

NEDA solution

Dissolve 0.5 g of NEDA in 500 ml of distilled water. This solution is stable for one month, if refrigerated and protected from light.

Hydrogen Peroxide solution

Dilute 0.2 ml of 30% hydrogen peroxide in 250 ml of distilled water. This solution may be used for one month, if, refrigerated and protected from light.

Stock nitrite solution

Dissolve 0.135 g of sodium nitrite in distilled water and dilute to 1000ml.

Standard nitrite solution

Dilute 1 ml of stock solution in 50 ml of distilled water (1 ml = 2 μg)

6.1.5 PROCEDURE

1. Pipette 0, 1, 3, 5, 7 ml of working nitrite solution. Dilute to 10 ml with absorbing solution (as sample plus)
2. Add 1 ml of diluted hydrogen peroxide solution and mix well.
3. Add 10 ml of Sulphanilamide solution.
4. Add 1.4 ml of NEDA and allow 10 min for colour development.
5. Prepare a blank in the same manner using 10 ml of unexposed absorbing reagent.
6. Read the absorbance at 540 nm against blank

6.1.6 CALCULATION

Calculate the volume of air samples as follows

$$V = \frac{F_i + F_f}{2} \, T_s \times 10^{-6}$$

V= volume of air sample, m^3

F_i=Air flow rate before sampling, cm^3/min

F_f= Air flow rate after sampling, cm^3/min

Ts=Sampling time, minutes

10^{-6}=Conversion cm to m^3

NO$_2$ concentration in air sample –

$$\mu g\ NO_2/m^3 = \frac{\mu g\ NO^-_2 \times Vs_f}{Va \times 0.82 \times Vt} \times D$$

$\mu g\ NO^-_2$ = NO^-_2 concentration in analysed sample

Va   = Volume of air sample, m^3

Vs_f = Final volume of sampling solution

Vt   = Aliquot taken for analysis

D   = Dilution factor (D=1 for no dilution, D=2 for 1:1 dilution)

0.82   = Sampling efficiency

6.2 DETERMINATION OF RESPIRABLE SUSPENDED PARTICULATE MATTER IN THE ATMOSPHERE

Sampling is done as per Indian Standard IS: 5182 (Part IV) - 1973. Air is drawn into the covered housing of RDS by means of a high flow rate blower at a flow rate of 1.13 to 1.70 m^3/min, that allows suspended particulates having diameters 100 μ to 0.1 μ to enter into the sampler. The air inside the sampler passes through a combination of cyclone and filter in two stages. At the first stage, the cyclone collects the bigger particles (particles in the size range of 10 μ to 100 μ). The rest of the particulate in the size range of 0.1 μ to 10 μ is collected over the filter surface. Thus the collection inside the container attached at the bottom of the cyclone gives the mass of PM_{10-100} and the collection over the filter paper represents the mass of PM_{10}. Glass-fibre filter papers are used due to its less affinity towards moisture absorption. The mass concentrations of PM_{10} and PM_{10-100} in μg/m^3 are computed by measuring the mass of collected particulates over the filter surface and inside the container respectively and volume of the air sampled.

Calculating PM$_{10}$

W_i = initial weight of filter (g)

W_f = final weight of the filter (g)

F_i = initial air flow rate (m^3/min)

F_f = final air flow rate (m^3/min)

T_i = initial time in time totalizer (hr)

T_f = final time in time totalizer (hr)

From the above data mass concentration of SPM is calculated as follows:

$$F_a = \text{average air flow rate} = \frac{F_i + F_f}{2} \ (m^3/min)$$

T = duration of sampling = $(T_f - T_i)$ x 60 (min)

Volume of air sampled, V (m^3)= F_a x T

$$\text{Mass concentration of PM}_{10} \ (\mu g/m^3) = \frac{(w_f - w_i) \times 10^6}{V}$$

Calculating PM$_{10\text{-}100}$

W_i = initial weight of the container (g)

W_f = final weight of the container (g)

Volume of air sampled, V (m^3) is same as that of the above, because the sampler is simultaneously sampling both the size fractions.

$$\text{Mass concentration of PM}_{10\text{-}100} \ (\mu g/m^3) = \frac{(w_f - w_i) \times 10^6}{V}$$

6.3 DETERMINATION OF SULPHUR DIOXIDE IN THE ATMOSPHERE

(Improved West and Gaeke method)

6.3.1 AIM

Determination of sulphur dioxide in the atmospheric air by Improved West and Gaeke method.

6.3.2 PRINCIPLE

Sulphur dioxide from ambient air is absorbed in a solution of potassium tetra chloro mercurate (TCM). Sulphur dioxide present in ambient air reacts with TCM solution and results in the formation of dichloro - sulphito mercurate complex. This complex is made to react with para rosaniline and formaldehyde to form an intensely coloured para rosaniline methyl sulphonic acid. The absorbance of the highly coloured azo dye is measured at 560 nm using spectrophotometer.

6.3.3 INTERFERENCES

Dichloro - sulphito mercurate complex is stable to strong oxidants such as ozone and oxides of nitrogen. The effect of interference by oxides of nitrogen is eliminated by the addition of sulphamic acid. Ozone is made to decompose by allowing the solution to stand prior to analysis, while trace metal interference is eliminated by the addition of EDTA in the absorbing reagent itself.

6.3.4 ABSORBING REAGENTS

0.04M potassium tetra chloro mercurate (TCM)

Dissolve 10.86 g mercuric chloride, 0.066 g EDTA and 6.0 g potassium chloride or 4.68 g sodium chloride in distilled water and dilute to 1000 ml. The pH of this reagent should be approximately 4. The absorbing reagent is normally stable for six months. If a precipitate forms, discard the reagent after recovering the mercury.

6.3.5 ANALYSIS

Sulphamic acid (0.6%)

Dissolve 0.6 g sulphamic acid in 100 ml distilled water. Prepare fresh daily.

Formaldehyde (0.2%)

Dilute 5 ml formaldehyde solution (36 to 38%) to 1 litre using distilled water. Prepare fresh daily.

Stock Iodine solution (0.1 N)

Place 12.7 g iodine in a 250 ml beaker. Add 40 g potassium iodide and 25 ml water. Stir until all is dissolved, then dilute to 1 litre using distilled water.

Iodine Solution (0.01 N)

Prepare approximately 0.01 N iodine solution by diluting 50 ml of stock solution to 500 ml using distilled water.

Starch Indicator Solution

Triturate 0.4 g soluble starch and 0.002 g mercuric iodide preservative with a little water and add the obtained paste slowly to 200 ml boiling water. Continue boiling until the solution is clear. Cool, and transfer to a glass-stoppered bottle.

Stock Sodium Thiosulphate Solution (0.1 N)

Prepare a stock solution by placing 25 g sodium thiosulphate pentahydrate in a beaker. Add 0.1 g sodium carbonate and dissolve using boiled and cooled distilled water, making the solution up to a final volume of 1 litre. Allow the solution to stand one day before standardizing.

To standardize, accurately weigh to the nearest 0.1 mg, 1.5 g primary standard potassium iodate (dried at 180°C). Dissolve and dilute to volume in a 500 ml volumetric flask. From the 500 ml flask, pipette 50 ml of iodate solution.

Add 2 g potassium iodide and 10 ml of 1 N hydrochloric acid and stopper the flask. After 5 minutes, titrate with stock thiosulfate solution to pale yellow. Add 5 ml of starch indicator solution and continue the titration until the blue colour disappears. Calculate the normality of the stock solution using

$$N = \frac{W \times 10^3 \times 0.1}{V \times 35.67}$$

N = Normality of stock thiosulphate solution

V = Volume of thiosulphate required, ml

W = Weight of potassium iodate, gm

35.67 – Equivalent weight of potassium iodate

Sodium thiosulphate titrant (0.01N) Dilute 100 ml of the stock thiosulfate solution to 1000 ml freshly boiled and cooled distilled water.

Standardized sulphite solution for preparation of working sulphite -TCM

Dissolve 0.3 gm of sodium meta bisulphate or 0.4 gm sodium sulphite in 500 ml of recently boiled and cooled distilled water. Sulphite solution is unstable. It is therefore, important to use water of the highest purity to minimize this instability. This solution contains the equivalent of 320 - 400 µg/ml of SO_2. The actual concentration of the solution is determined by adding excess iodine and back-titrating with standard sodium thiosulfate solution.

To back-titrate, pipette 50ml of the 0.01 N iodine solution into each of the two 500 ml iodine flasks namely A & B. To flask A (blank), add 25 ml of distilled water and into flask B (sample), pipette 25 ml sulphite solution. Stopper the flask and allow to react for 5 minutes. By means of a burette, containing standardized 0.01 N thiosulfate solution, titrate each flask in turn, to pale yellow. Then add 5 ml starch solution and continue the titration until the blue colour disappears.

Working Sulphite –TCM solution

Pipette 2 ml of the standard solution into a 100 ml volumetric flask and bring to the mark with 0.04 M TCM. Calculate the concentration of SO_2 in the working solution.

$$\mu g\ SO_2\ /ml = \frac{(A-B)\ (N)\ (32000)}{25} \times 0.02$$

A = Volume of Thiosulphate for blank, ml

B = Volume of Thiosulphate for sample

N = Normality of thiosulphate solution

32,000 = milli equivalent weight of SO_2 /µg

25 = volume of standard sulphite solution, ml

0.02 = Dilution factor

This solution is stable for 30 days if kept at 5°C

Pararosaniline stock solution

Dissolve 0.5 g specially purified para rosaniline (PAR) in 100 ml distilled water. Keep for 2 days and filter the solution. The filtered solution is stable for 3 months if stored in refrigerator.

Para rosaniline working solution

Take 10 ml of stock PAR solution in a 250 ml volumetric flask. Add 15 ml conc. HCl and make up to volume with distilled water.

Determination

1. Transfer the sample from the impinger tube to a beaker.
2. Prepare a reagent blank by adding 10 ml of unexposed TCM solution to a 25 ml volumetric flask.
3. Prepare a control solution by measuring 2 ml of working sulphite TCM solution and 8 ml of TCM solution into a 25 ml volumetric flask.
4. Add 1 ml of sulphamic acid to each flask and allow it to stand for 10 minutes to destroy nitrite from oxides of nitrogen.
5. Then add 2 ml of formaldehyde and 2 ml of the dye to each flask.
6. Allow the mixture to react for 30 min.
7. After 30 min but before 60 min, determine the absorbance of the sample using spectrophotometer.
8. The absorbance should be taken at 560 nm.
9. The same procedure is adopted for the determination of the absorbance of the reagent blank.

Calibration curve

1. Take 10, 9, 8, 7, 6, 5 ml of the samples in beakers.
2. Add 0, 1, 2, 3, 4, 5 of working sulphite TCM solution in to the beaker.
3. Add 1 ml of sulphamic acid reagent
4. Add 2 ml of formaldehyde
5. Add 5 ml of dye in each beaker.
6. Bring the level in each beaker to 25 ml by adding distilled water.
7. Determine the absorbance of solution in each beaker using spectrophotometer.
8. Plot the absorbance against the total concentration in µg SO_2 for corresponding solution.
9. Find the slope of the straight line obtained.
10. The reciprocal of the slope is taken as Bg and it is used in the calculation.

6.3.6 Calculation

Conversion of volume: Convert the volume of air sampled to the volume at reference conditions of 25° and 760 mm of Hg.

$$V_R = V \times \frac{P}{760} \times \frac{298}{t+273}$$

V_R = Volume of air at 25° C and 76O mm of Hg, litres

V   = Volume of air sampled, litres.

P   = Barometric pressure, mm of Hg.

T   = average temperature of air sample, °C

Sulfur dioxide concentration:

When sulphite solutions are used to prepare calibration curve, compute the concentration of sulphur dioxide in $\mu g/m^3$ in the sample as follows.

$$\mu g \, SO_2 /m^3 = \frac{(A-Ao) \, (10^3) \, (Bg)}{V_R} \times D$$

A = Absorbance of the sample

Ao = Reagent blank absorbance

10^3 = Conversion of litres to cubic metres

V_R = Volume of the air passed through the absorbance solution

Corrected to 25° C and 760 mm of Hg, litres.

Bg = Calibration factor, $\mu g/$ absorbance unit

D   = Dilution factor

Concentration of SO_2 in $\mu g/m^3$ in the sample is calculated as follows

$$C = \frac{(A-Ao)\,(10^3)\,(Bg)}{V}$$

A = Absorbance of the sample

Ao = Reagent blank absorbance

10^3 = Conversion of litres to cubic metres

Bg = Calibration factor, μg/ absorbance unit

V   = Volume of air sampled in litres

National Ambient Air Quality Standards

Pollutants	Time weighted Average	Concentration in ambient air ($\mu g/m^3$)		
		Industrial areas	Residential, Rural & Other areas	Sensitive areas
Sulphur dioxide (SO₂)	Annual Average	80	60	15
	24 hours	120	80	30
Oxides of Nitrogen (NOₓ)	Annual Average	80	60	15
	24 hours	120	80	30
Suspended Particulate Matter (SPM)	Annual Average	360	140	70
	24 hours	500	200	100
Respirable Particulate Matter (RPM) size less than 10 microns	Annual Average	120	60	50
	24 hours	150	100	75
Carbon Monoxide (CO)	8 hours	5000	2000	1000
	1 hour	10000	4000	2000

(CPCB. 1997: Ambient air quality status and trends in Delhi (1989 - 1993).

NAAQMS/9/1996-97, CPCB publications, Delhi, India)

7) ANALYSIS OF METEOROLOGICAL DATA

7.1 INTRODUCTION

This section describes the analyses of meteorological parameters for diffusion climatology and surface observations. Appropriate formats for presentation of data are also given. Specifications of the meteorological equipments and the list of suppliers are given in sections 7.10 to 7.11.

7.2 ANALYSIS OF WIND TRACE

1. Take an average of the wind direction trace from hour beginning to hour end, e.g. for 00-01 h, 01-02 h,......., 23-00 h and record hourly wind direction in degrees.

2. Analyse for wind speed in (m/sec) for sensors giving analog output. For places where contact type anemometers are used, wind speed be recorded in km/h.

3. Find the hourly wind direction range i.e. the difference of maximum and minimum wind direction trace.

4. This gives a set of wind speed, wind direction and wind direction range for each hour.

5. In situations, when it is not possible to easily take an eye average due to frequent large variations in wind direction trace, it should be classified as variable 'VAR'.

6. When hourly wind speed is found to be less than 3km/h, it should be termed as 'calm' for wind direction. However, the hourly wind speed observed during the hour be also recorded.

7. These hourly sets of observations; hourly wind   speed, wind direction and wind direction range form the raw data for further analysis.

7.3 INPUT WIND DATA FOR JOINT FREQUENCY DISTRIBUTION (JFD)

7.3.1 CLASSIFICATION OF WIND SPEED CLASSES

The wind speed classes are made as given in Table - 7.1.

Table - 7.1

S No.	Wind Speed Class	Mid Values of Wind Speed Class
1	less than 3 km/h	--
2	3 km/h - 5 km/h	4.0 km/h
3	6 km/h - 11 km/h	8.5 km/h
4	12 km/h - 19 km/h	15.5 km/h
5	20 km/h - 29 km/h	24.5 km/h
6	30 km/h - 38 km/h	34.0 km/h
7	39 km/h - 50 km/h	44.5 km/h
8	51 km/h - 61 km/h	56.0 km/h
9	62 km/h - 74 km/h	68.0 km/h
10	75 km/h - 87 km/h	81.0 km/h
11	87 km/h - 98 km/h	92.5 km/h

7.3.2 COMPASS WIND DIRECTION

Important Explanation

1. Wind direction is the direction from which the wind is blowing, e.g., Wind direction North (N) means wind is blowing from 'North'(N) and going towards 'South' (S).

2. 0° -360° have been divided into 16 sectors of 22.5 degrees each. Each compass direction has spread of 11.25 degrees on either side of principal direction ray, e.g. Wind direction, North (N) denotes all the hourly averaged wind direction observations between 348.76^o and 11.25^o. Conversion of wind direction data in degrees be made in sixteen compass directions and are tabulated in table - 7.2.

3. Take concurrent data of hourly wind speed and wind direction for preparation of JFD table.

4. Assign tally marks for each hourly concurrent wind speed and compass direction to which the concurrent wind speed and wind direction belong.

5. Continue for each hourly set of wind speed and wind direction.

6. Find the number of observations missing. The hourly observation is termed missing if any of the following three cases arise:

   a) Wind speed data missing during the hour, OR

   b) Wind direction data missing during the hour, OR

   c) Wind speed and wind direction data both missing during the hour.

7. Find the total number of observations available (Total possible hourly observations during the month minus total missing observations).

8. Find the percent frequencies of occurrences of each wind speed class and compass direction, calm and variable using

$$\frac{\text{Number of occurrences}}{\text{Total observations available}} * 100$$

9. Tables - 7.3 & 7.4 give convenient proforma of JFD for keeping the records for number of occurrences and percent frequency of occurrence in a month respectively.

10. From the monthly JFD table of number of occurrences: quarterly, annual or seasonal JFD can be generated by summing up the number of occurrences corresponding to each wind speed class and wind direction, total possible hourly observations and total missing data and therefrom JFD in percent be generated.

Table - 7.2 CONVERSIONS OF WIND DIRECTION DATA IN DEGREES

1.00	North (N)	348.76 - 11.25
2.00	North North-East (NNE)	11.26 - 33.75
3.00	North-East (NE)	33.76 - 56.25
4.00	East North-East (ENE)	56.26 - 78.75
5.00	East (E)	78.76 - 101.25
6.00	East South-East (ESE)	101.26 - 123.75
7.00	South-East (SE)	123.76 - 146.25
8.00	South South-East (SSE)	146.26 - 168.75
9.00	South (S)	168.76 - 191.25
10.00	South South-West (SSW)	191.26 - 213.75
11.00	South-West (SW)	213.76 - 236.25
12.00	West South-West (WSW)	236.26 - 258.75
13.00	West (W)	258.76 - 281.25
14.00	West North-West (WNW)	281.26 - 303.75
15.00	North-West (NW)	303.76 - 326.25
16.00	North North-West (NNW)	326.26 - 348.75

Table 7.3 JOINT FREQUENCY DISTRIBUTION OF
HOURLY WIND SPEED AND DIRECTION

STATION: ESML NAPS.   HEIGHT: 30 m   PERIOD: AUGUST 1994

DIRECTION				WIND SPEED (km/h)						
	< 3	3-5	6-11	12-19	20-29	30-38	39-50	51-61	62-80	TOTAL
CALM	41	0	0	0	0	0	0	0	0	41
N		9	25	4	0	0	0	0	0	38
NNE		11	64	35	0	0	0	0	0	110
NE		12	53	35	1	0	0	0	0	101
ENE		11	20	8	1	0	0	0	0	40
E		4	5	1	0	0	0	0	0	10
ESE		5	7	0	0	0	0	0	0	12
SE		8	11	2	0	0	0	0	0	21
SSE		9	19	1	0	0	0	0	0	29
S		3	15	16	0	0	0	0	0	34
SSW		7	24	6	0	0	0	0	0	37
SW		6	19	12	0	0	0	0	0	37
WSW		6	18	15	0	0	0	0	0	39
W		6	1	0	0	0	0	0	0	7
WNW		12	9	0	0	0	0	0	0	21
NW		12	20	1	0	0	0	0	0	33
NNW		26	30	1	0	0	0	0	0	57
VAR		26	12	1	0	0	0	0	0	39
TOTAL	41	173	352	138	0	0	0	0	0	706

ICARD% = 744   IC%   = 744   ICARD% - MISS% = 706   MISS% = 38

NM%   = 706 ACTUAL% = 706   VCOUNT% = 39

MAXIMUM WIND SPEED = 22   MINIMUM WIND SPEED = 1

Table 7.4 JOINT FREQUENCY DISTRIBUTION OF

HOURLY WIND SPEED AND DIRECTION (%)

STATION: ESML NAPS.   HEIGHT: 30 m   PERIOD: AUGUST 1994

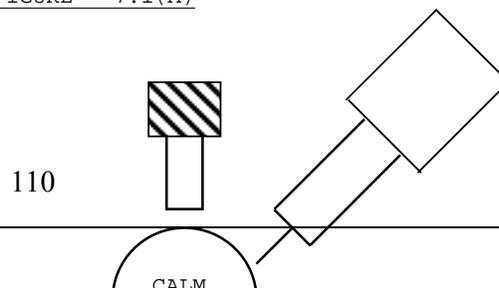| DIRECTION				WIND SPEED (km/h)						
	< 3	3-5	6-11	12-19	20-29	30-38	39-50	51-61	62-80	TOTAL
CALM	5.81	0	0	0	0	0	0	0	0	5.81
N		1.27	3.54	0.57	0	0	0	0	0	5.38
NNE		1.56	9.07	4.96	0	0	0	0	0	15.58
NE		1.7	7.51	4.96	0.14	0	0	0	0	14.31
ENE		1.56	2.83	1.13	0.14	0	0	0	0	5.67
E		0.57	0.71	0.14	0	0	0	0	0	1.42
ESE		0.71	0.99	0	0	0	0	0	0	1.7
SE		1.13	1.56	0.28	0	0	0	0	0	2.97
SSE		1.27	2.69	0.14	0	0	0	0	0	4.11
S		0.42	2.12	2.27	0	0	0	0	0	4.82
SSW		0.99	3.4	0.85	0	0	0	0	0	5.24
SW		0.85	2.69	1.7	0	0	0	0	0	5.24
WSW		0.85	2.55	2.12	0	0	0	0	0	5.52
W		0.85	0.14	0	0	0	0	0	0	0.99
WNW		1.7	1.27	0	0	0	0	0	0	2.97
NW		1.7	2.83	0.14	0	0	0	0	0	4.67
NNW		3.68	4.25	0.14	0	0	0	0	0	8.07
VAR		3.68	1.7	0.14	0	0	0	0	0	5.52
TOTAL	5.81	24.5	49.86	19.55	0.28	0	0	0	0	100

7.4 WIND ROSE

Wind rose is a pictorial way of representing the distribution of prevailing wind

direction pattern or wind speed and wind direction pattern. It is constructed using JFD expressed as percent as explained below.

7.4.1 WIND ROSE FOR WIND DIRECTION

1. Draw a circle of radius 1.0 cm, and write CALM and percent occurrence of calm in the interior of the circle.

2. Take a point on the circumference vertically above the centre of circle to mark zero degree representing wind direction 'North'.

3. From this reference point, mark another point on the circumference clockwise such that the degree measure of the arc is 22.5^o indicating the wind direction NNE. Similarly, go on marking the points on the circumference clockwise to get arcs of degree measure 22.5^o each to indicate wind directions NE, NNE, E, ..., WNW. In this manner, the directions E, S and W will be 90°, 180° and 270° respectively from NORTH taken as zero degree.

4. Select a convenient scale say 1.0 cm = 2.0 % of frequency of occurrence.

5. Calculate the line segments representing the frequency of occurrence of each wind direction.

6. Draw the line segments starting from the points marked on the circumference for corresponding wind direction. For drawing the line segment, the centre of the circle must be taken as second point.

7. As an illustration (see Figure 7.1(A)), four line segments have been drawn using data of Table - 7.4, last column under 'total' for the wind directions N, S, WSW and NW using, 1 cm = 4 % of frequency of occurrence.

FIGURE - 7.1(A)

110
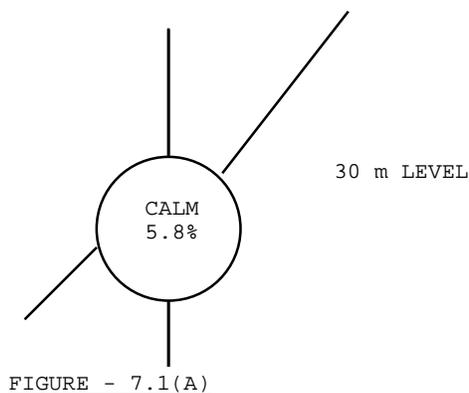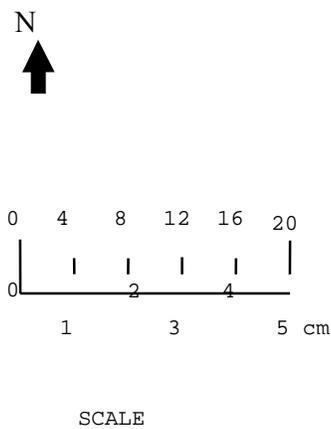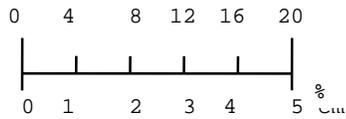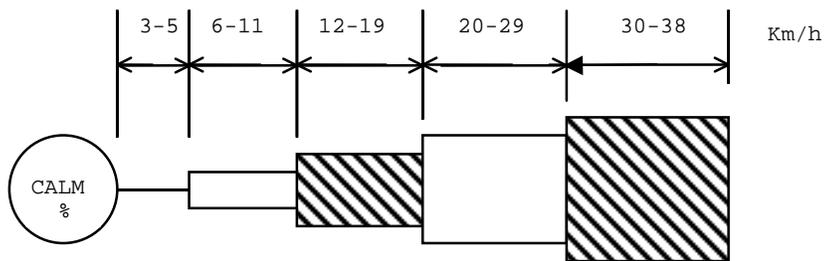
Figure - 7.1(B)

Figure - 7.1 Illustrations for Wind Roses

7.4.2 WIND ROSE FOR WIND SPEED AND WIND DIRECTION

1. Follow steps (1) to (4) as in 7.3.1 for drawing wind direction wind rose.

2. Calculate line segments for each wind speed class for a given wind direction.

3. Make a scheme to differentiate the wind speed classes for all the wind directions. A convenient scheme is; line followed by alternate plain and shaded blocks of increased width as shown below.
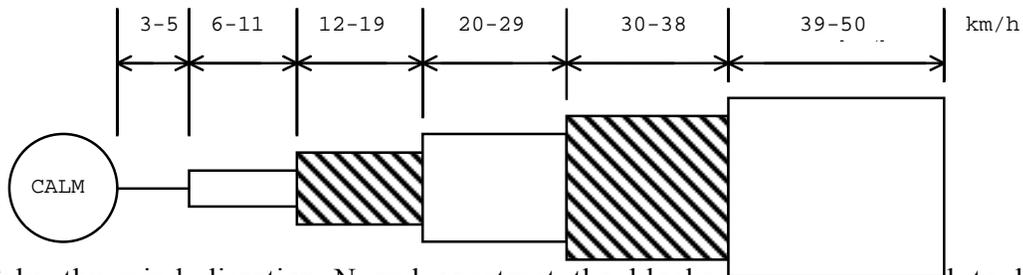
4. Take the wind direction N and construct the blocks of lengths equal to line segments calculated in step (ii), and follow for other wind directions in similar way.

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5. As an illustration (see Figure 7.1(B)), four blocks have been drawn using data of Table - 5.4 for wind directions N, S, WSW and ENE.

7.5 TRIPLE JOINT FREQUENCY DISTRIBUTION OF HOURLY WIND SPEED, WIND DIRECTION AND ATMOSPHERIC STABILITY (TJFD)

For computation of atmospheric dilution factors and doses in public domain, monthly Triple Joint Frequency Distribution of hourly wind speed, wind direction and atmospheric stability classes be prepared and summed up for computation of annual TJFD. Wind speed and wind direction refer to height of release. Atmospheric stability be ascertained from 10 m height data, depending upon the availability of instruments.

7.5.1 IDENTIFICATION OF ATMOSPHERIC STABILITY

Identification of Pasquill stability classes is made for each hour depending upon the availability of equipments at site. Three approaches, which can be conveniently adopted, are given below:

1. In this approach, identification of Pasquill's stability classes is done using hourly standard deviation of horizontal wind direction fluctuations, r_θ. In actual practice, hourly wind direction range at 10 m height may be used. The r_θ and spread of wind direction range are given in Table - 7.5

2. Table - 5.6 gives the identification of Pasquill's stability classes using wind speed at 10 m height, solar radiation and cloud cover. (Source: IAEA Safety Series, 50-SG-S3, 1980, p66).

3. Table - 7.7 gives the identification of Pasquill's stability classes using wind speed at 10 m height, solar radiation and night net radiation. (Source: IAEA Safety Series, 50-SG- S3, 1980, p67)

   i. Find the stability category for each hour, using one of the above approaches.

   ii. 5.2 and section(1-7) give a set of hourly Wind Speed ,Wind Direction and Atmospheric Stability data for a given month.

   iii. Triple Joint Frequency Distribution of Hourly concurrent data of Wind Speed, Wind Direction and Atmospheric Stability can be generated in a similar way as for JFD.

   iv. A convenient proforma of generation of TJFD is given in Table 5.8

v. These monthly TJFD's are used to generate the annual TJFD, which is normally required, as input to calculate atmospheric dilution factor and for computation of doses in public domain.

Table 7.5 Identification of Pasquill's Stability Classes
Using Wind Direction Fluctuations

Pasquill's Stability Categories	Standard Deviation of wind direction fluctuations	Spread of Wind Direction Range
A	25.0^o	$> 135^o$
B	20.0^o	$105^o - 135^o$
C	15.0^o	$75^o - 105^o$
D	10.0^o	$45^o - 75^o$
E	5.0^o	$23^o - 45^o$
F	2.5^o	$< 23^o$

Table 7.6 Modified Stability Classification Table Using
Solar Radiation and Cloud Amount

Wind speed U(m/s)	Stability Class ,day, with solar radiation R_D (Langleys.h^{-1})			Stability Class, day and night with cloud(8/10 to 10/10)	Stability Class, night, with	
	$R_D \geq 50$	$50 < R_D \leq 25$	$R_D > 50$		Upper cloud (5/10 to 10/10) middle, low cloud (5/10 to 7/10)	Cloudiness (0/10 to 4/10)
U < 2	A	A-B	B	D	-	-
2 <= U < 3	A-B	B	C	D	E	F
3 <= U < 4	B	B-C	C	D	D	E
4 <= U < 6	C	C-D	D	D	D	D
U≥6	C	D	D	D	D	D

Notes:

1. In the original table by Pasquill, insolation is expressed qualitatively, but in this table modified equivalents are shown quantitatively.

2. 'Night' refers to a period from one hour before sunset to one hour after sunrise.

3. Neutral class 'D' is applied when lower cloudiness is 8/10 to 10/10 both in daytime and at night regardless of wind speed.

4. Neutral class 'D' is applied for a period of one hour before and after 'Night' regardless of cloud condition.

5. 1 Langley = 1 cal.cm^{-2} = 4.187 J.cm^{-2}.

Table 7.7 Modified Stability Classification Table Using
Solar Radiation and Night Net Radiation, With Wind Speed

Wind speed U(m/s)	Stability Class ,day, with solar radiation R_D (Langleys.h^{-1})				Stability Class, day and night with cloud (8/10 to 10/10)	Stability Class, night, with Net radiation R_N(Langleys.h^{-1})		
	R_D >=50	50>R_D≥25	25>R_D≥12.5	12.5>R_D		R_N >-1.8	-1.8≥R_N>-3.6	-3.6≥R_N
U < 2	A	A-B	B	D	D	D	-	-
2 <= U < 3	A-B	B	C	D	D	D	E	F
3 <= U < 4	B	B-C	C	D	D	D	D	E
4 <= U < 6	C	C-D	D	D	D	D	D	D
U≥6	C	D	D	D	D	D	D	D

Notes:

1. Radiation from the ground upward is taken as negative in the calculation of R_N. The value of R_N is usually negative but sometimes it is positive.

2. The values of solar radiation and night net radiation are the average of a 10 min period before the observation time.

3. 'Day' refers to the period from sunrise to sunset, and night refers to sunset to sunrise.

4. 1 Langley = 1 cal.cm^{-2} = 4.187 J.cm

Table - 7.8 TRIPLE JOINT FREQUENCY DISTRIBUTION OF HOURLY WIND SPEED, WIND DIRECTION AND ATMOSPHERIC STABILITY

STATION: ESM LAB, NAPS.   HEIGHT: 30 METER   PERIOD: --------

WS Class (km/h)	ATMS STAB	N	NNE	NE	ENE	E	ESE	SE	SSE	S	SSW	SW	WSW	W	WNW	NW	NNW	VAR	TOTAL
3 TO 5	A																		
	B																		
	C																		
	D																		
	E																		
	F																		
6 TO 11	A																		
	B																		
	C																		
	D																		
	E																		
	F																		
12 TO 19	A																		
	B																		
	C																		
	D																		
	E																		
	F																		
20 TO 29	A																		
	B																		
	C																		
	D																		
	E																		
	F																		

TOTAL NUMBER OF OBSERVATIONS=

TOTAL NUMBER OF CALMS   =

7.6 SOLAR RADIATION

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1. Find the Multiplication Factor, say 'X', in   Langley/h/chart division, using sensitivity of the solarimeter expressed in mV/Langley/min as supplied by the manufacturer.

2. Mark the date and hour of the day on the solarimeter chart trace keeping in view the pre-set chart speed and power supply failure.

3. Find the average number of chart divisions during the hour, call it 'Y'.

4. Calculate XxY to know the solar radiation during that hour in Langley

5. Explanation: Suppose solar radiation is recorded on chart having 100 equally spaced divisions for full range of the recorder set for 20 mV range, and the average chart trace between 10.00 - 11.00 hours is Y = 30 chart   divisions.

The sensitivityof the solarimeter given by manufacturer is 8.1224 mV/Langley/min.

 Now one chart division corresponds to 20 mV / 100 = 0.2 mV.

$$X \quad = \quad \frac{0.2 \text{ mV/Chart division}}{8.1224 \text{ mV/Langley/min}} \times 60 \text{ (min/h)}$$

$$= \quad 1.48 \text{ Langley/h/chart division.}$$

Solar radiation falling on horizontal surface during

10.00 - 11.00 hours = 1.48x 30 = 44.4 Langley.

Useful conversion factors:

$$\text{Langley /min} \quad = \quad 1 \text{ cal/cm}^2\text{/min}$$
$$= \quad 4.187 \text{ J/cm}^2\text{/min}$$
$$= \quad 697.833 \text{ W/m}^2$$

7.7 AMBIENT AIR TEMPERATURE

1. Mark the date and time on the ambient air temperature trace from the thermohygrograph setting.

2. Read temperature reading at hour beginning and record it.

3. Convert the readings into ^{o}C (degree Celsius) in case   the chart markings are in the ^{o}F (degree Fahrenheit).

7.8 AMBIENT AIR RELATIVE HUMIDITY

1. Mark the date and time on the ambient air relative humidity trace from the thermohygrograph setting.

2. Read relative humidity reading at hour beginning in percent and record it.

3. For instruments which record dry and wet bulb temperature, read the dry and wet bulb temperature as in 7.6(3). Find the depression of wet bulb and use appropriate psychrometry tables to read the relative humidity.

7.9 RAINFALL

1. Mark the date and time on the rainfall chart of self recording type rain guage.
2. Note the hour beginning reading say, 'b' mm.
3. Count the number of times the rainguage has siphoned off to zero after siphoned off of step (ii), say 'n' times.
4. Read the chart reading at the end of the hour say 'e' mm.
5. Find (10 - b) + (10 x n) + e. This gives the hourly rainfall in mm.
6. Find the daily and cumulative rainfall of the year.

7.9.1 RAINFALL RATE

1. To obtain average intensity of rainfall for a time interval, divide the total rainfall in mm during the period, by the number of hours during that period. If R_1 mm is the rainfall upto T_1 hours and R_2 mm is the rainfall upto T_2 hours, then the average intensity of rainfall in (T_2 - T_1) hours is equal to $(R_2 - R_1)/(T_2 - T_1)$, mm/h. In the illustration (A) given below the average intensity of rainfall or rainfall rate between 01.00 and 04.00 hrs is (7.0 - 3.0)/(04 - 01) = 1.33 mm/h.

2. To obtain the instantaneous intensity of rainfall at any instant, T; draw a perpendicular at T to meet the rainfall trace at point 'p' as in the illustration (B) given below. On either side of point 'p' and very near to 'p', chose two points A & B equidistant from P. Join AB and extend it to meet the zero rainfall line in T'. The intensity of rainfall at the instant 'T', is given by the ratio PT/TT'. Using the values as given in the illustration (B), the intensity of rainfall at 04.15 hours is 6/1.75 = 3.43 mm/h.

7.10 METEOROLOGICAL EQUIPMENTS

7.10.1 WIND SPEED AND WIND DIRECTION

Wind recording system consisting of low threshold anemometer and wind vane mounted on cross arm and having the following specifications.

7.10.2 LOW THRESHOLD ANEMOMETER

Sensor : 3 cup assembly, polycarbonate, 7 cm dia

Transducer : High frequency tachometer (DC generator)

Output : 12V square wave, 223 Hz at 80 km/h wind speed (1V DC at 160 km/h)

Range : 0 - 160 km/h (0 - 100 km/h. & 0 - 160 km/h, switch selectable)

Accuracy : $\pm$ 0.25 km/h.

Threshold : less than 1.6 km/h.

Materials : Aluminium and Stainless steel

7.10.3 LOW THRESHOLD WIND VANE

Sensor : Counterbalanced tail

Transducer : 5K ohms potentiometer, single wiper, having $\pm$0.5% linearity.

Range : 0 - 360° or 0 - 540° switch selectable

Accuracy : $\pm$2°

Threshold : 1.0 km/h or less

Damping ratio : 0.4

Materials : Aluminium and Stainless steel

7.10.4 WIND SPEED TRANSLATOR UNIT

Range : 0 - 100 km/h. & 0 - 160 km/h., switch selectable.

Output : 0 - 1 mA/0 - 5 V linear for the two ranges.

Accuracy : 1% FSD

Calibration : Provision for calibration check at about 33% & 67% of
the two ranges.

Power : 230V AC, 50 Hz with battery backup 12V DC in case of power failure

Mounting : NIM module or flush panel

7.10.5 WIND DIRECTION TRANSLATOR UNIT

Range : 0 - 360° or 0 - 540° switch selectable

Output : 0 - 1 mA/0 - 5 V linear for the two ranges

Calibration check: Zero and full span as well as 25% and 50% portion of the range.

Power : 230V AC, 50 Hz with battery backup 12V DC in case of power failure

Mounting   : NIM module or flush panel

7.10.6   WIND RECORDER

Strip chart recorder for recording wind speed and wind direction (singly or both on the same chart) Capable of accepting inputs from 5.10.2 and 5.10.3

Chart speed   :   2.5 cm, 5.0 cm, 7.5 cm and 10.0 cm per hour and per minute adjustable by lever switch or change of gears

Response   : less than 1 second

Power   : 230V AC, 50 Hz with battery backup 12V DC in case of power failure

7.10.7   ATMOSPHERIC TEMPERATURE

7.10.7.1   ATMOSPHERIC TEMPERATURE RECORDING SYSTEM

Sensor   : 99.99% pure platinum wire encased in 10 cm stainless steel housing.

Resistance   : 100 ohms at 0^oC intermatching of different resistance thermometers within 0.1%, gold   plated terminals.

Time constant   : less than 10 seconds

Accuracy   : less than 0.1 ^{o}C

7.10.7.2   RADIATION SHIELD

Motor-aspirated radiation shield for above platinum resistance thermometer, highly reflective paint.

Air speed   : About 1.8 m/sec, 0.7 m^3/minute free air   delivery.

Radiation error   : 0.05 ^{o}C during maximum aspiration and   full sun.

Material   : Aluminium

Power Input   : 230V AC and 50 Hz.

Mounting   : Suitable fixture for mounting on tower face.

7.10.7.3   TEMPERATURE TRANSLATOR UNIT

Temperature translator unit compatible with the above sensor and having provision of accepting eight number of such inputs.

RT excitation current : less than 4 mA

Temperature range   : 0 - 50°C

Calibration Accuracy : 0.1% or better

Output   : 4-20 mA/0-5V switched/0-1V/0-5V linear for 0 - 50°C range and compatible with   potentiometric strip chart recorder/data   acquisition system

Accuracy   : 1 % FSD

Sensor Cable Length : 300m - 500m

Calibration check : Calibration facility to check for 10°C, 25°C, and 40°C

Mounting   : NIM modular / Flush panel

 Power   : 230V AC, 50 Hz with battery backup 12V DC in case

         of power failure.

7.10.7.4 TEMPERATURE RECORDER

Six point multichannel strip chart recorder compatible with above systems for recording of atmospheric temperature.

Impedance   : 100 K ohms (approximately)

Input range   : 0-5V and 4-20 mA corresponding to 0-50°C

         varying linearly and compatible with the temperature

         translator unit.

Recording system : Dotting in six different colours with the identification,

+,   followed by input No.(+1,+2,+3 etc.)

Chart speeds   : 2.5 cm, 5.0 cm, 7.5 cm/h switch selectable

Operation   : 230V AC, 50 Hz with battery backup 12V DC in case of

         power failure

7.10.8 AIR TEMPERATURE AND RELATIVE HUMIDITY

7.10.8.1 THERMOHYGROGRAPH

Thermohygrograph for continuously recording of ambient air temperature and relative humidity on daily/weekly basis on a double scale chart and having the following specifications

Sensor	Temperature	Relative Humidity of well
	Aged bimetallic hellical strip	treated bundle of human hair
Range Accuracy	5 ^{o}C to 50°C (normal) ± 0.5 ^{o}C	0 - 100 % ± 5% in the range of 20 to 95 %

Recording chart drum at constant speed by a quartz clock drum running on 1.5V dry battery selectable complete rotation of drum in one day or one week 26 hrs/176 hrs.)

Standard accessories

1. Daily and weekly charts with temperature range -5 to 50°C and relative humidity range 0 to 100%

2. Replacement hair bundle

3. Replacement cartridge pen

Combined PT1000 platinum resistance thermometer and integrated circuit(IC) humidity sensor coupled to a data   logger can also be used to measure temperature and RH.

7.10.8.2 INSTRUMENT SHELTER

Stevenson screen /Instrument shelter to house thermohygrograph, thermometers etc. with double roof protection against solar radiation and rain.

Material	:	Clear pine
Paint	:	Primer and white latex (three coats)
Thermometer mount	:	Interior cross board
Ventillation	:	Louvered on all sides and vented through the bottom to provide ambient conditions inside.
Size	:	762 mm (W) x 508 mm (D) x 813 mm (H)
Metal legs	:	1.53 m Aluminium having cross arms, easy to assemble
Locking	:	Door should have locking arrangement

7.10.9 RAINFALL

7.10.9.1 SELF RECORDING RAINGAUGE

Self recording raingauge for recording of rainfall with automatic syphoning system after 10 mm of rainfall, Base and collector made from rugged fiber reinforced plastic with gunmetal collector rim. Collector rim dia 203 mm. Chart dimension 0.5 mm of rainfall. Quartz standard drum movement using 1.5V cell and having facility to change speed from daily to weekly.

Accessories

1) Chart with 0.5 mm graduation (0-10 mm)

2) Ink bottle

3) Recording pen

4) Quartz clock drum

7.10.9.2 NON-RECORDING RAINGAUGE

Base and collector made from fiber reinforced plastic and fitted with Aluminum locking rings. Collector rim made of gunmetal and having 200 cm^2 area

Accessories

1) 2 liter plastic bottle

2) Measuring cylinder 20 mm capacity

7.10.10 ATMOSPHERIC PRESSURE

7.10.10.1 BAROGRAPH

Barograph for recording of atmospheric pressure with temperature compensation

Sensor	: Aneroid bellow (Beryllium -copper /copper- bronze)
Recording range	: 940 mb - 1025 mb
Accuracy	: $\pm$ 0.1 mb (typical),$\pm$ 0.2 mb (maximum)
Sensitivity	: $\pm$ 0.1 mb (typical),$\pm$ 0.2 mb (maximum)
Temperature compensation	: Bimetallic strip
Clock type	: 1.5 V DC battery operated quartz
Drum rotation	: Daily / Weekly (inter convertible)
Pen type	: Disposable fibre tip
Smallest division on chart	: 0.5 mb

Accessories

1) Charts daily/weekly, smallest division 0.5 mb

2) Disposable fiber tips

3) Spare clock assembly

7.10.10.2 FORTIN'S BAROMETER

Mercurial barometer Fortin type with attached thermometer mounted on mahogany base and having mm/mb scale: least count: 0.05 mm Hg / 0.1 mb. Range: 646 to 800 mm Hg.

7.10.11 GLOBAL SOLAR RADIATION - PYRANOGRAPH

Mechanical pyranograph for continuous recording of the intensity of global solar radiation (direct + diffuse)

Sensor	: black and white bimetallic strip
Spectral response	: 0.3 to 3.0 microns
Recording range	: 0-2.5 ly/min or 0-1500 w/m^2
Graduation on chart	: 0.05 ly / min or 30w/m^2

Lag coefficient   : about 5 min

Clock type   : 1.5 V DC battery operated quartz drum rotation

                                 26 hours / 176 hours

Pen type   : Cartridge

Levelling   : 3 adjustable feet and bull's eye level

Accessories

Spare parts kits- standard Charts

1) 0 - 2.5 ly/min, 176 hrs

2) 0 - 2.5 ly/min, 24 hrs

3) 0 - 1500 w/m^2, 176 hrs

4) 0 - 1500 w/m^2, 24 hr

7.10.12   NET RADIOMETER

Net radiometer for the measurement of difference between incoming and outgoing radiation complete with mounting arm and cable.

Sensor   : 32   junction,   copper-constantan   thermopile   in   contact   with   two   blackened   copper   plates   one   facing   upward   to   absorb   the   incoming   radiation   and   other   facing   downward   to   absorb   outgoing   radiation.

Sensitivity   : about 11 micro volt/watt/m^2

Spectral response   : 0.3 to 60 microns

Internal resistance   : 5 ohms

Time constant   : 12 seconds

Range   : -500 to 1500 w/m^2

Wind shields   : 28 mm dia lupolene domes replaceble in the field

Desiccant   : Silica gel desiccant in attached cylinder for

                        absorption of the moisture in the net radiometer.

Recorder   : Single pen potentiometric strip chart   recorder

                        compatible with the above chart   speed 2.5 and

                         5.0 cm/h switch selectable

Chart range   : (1) -0.5 to 2.5 ly/min

                          (2) -500 to 1500 w/m^2

7.10.13 METEOROLOGICAL DATA ACQUISITION SYSTEM

20 (twenty) input meteorological data acquisition and analysis system compatible to IBM PC with user specified inputs and software.

7.11 LIST OF SUPPLIERS OF METEOROLOGICAL EQUIPMENTS

1. M/S Weather Measure,

   Division of Qualimetrics Inc. 1165

   National Drive,

   Sacramento, California 95834 USA

2. Climatronics Corporation, 140 wilbur place, PO Box 480,

   Bohemia New York - 11716 USA

3. RM Young Company,

   2801 AERO Park Drive, Traverse City,

   MT 49684, USA.

4. Science Associates Inc.,

   230 Nassau Street,

   Box 230, Princeton,

   New Jersy 8540 USA

5. Wilh. Lambrecht KG

   34 gottingen

   West Germany.

6. KIPP AND ZONEN

   Mercuriusweg

   PO Box 507

   DELFT-HOLLAND

7. Pollution Equipments & Controls

   A-3/4 Local Shopping Centre

   Near St. Marks School

   Janakpuri, New Delhi- 110058

8. M/S Dynalab,

   C-3/G-2 Brahma Memories

   Bhonsale Nagar

   Pune 411007

9. India Meteorological Deptt.

Instrument Division

Ganesh Khind

Pune 411005

10. Doon Engineers (Pvt.) Ltd.

12 New Road,

Dehradun, U.P.

11. Lawrence and Mayo Pvt. Ltd.

Scientific and Engineering Instruments Division

274, DN Road, Bombay

12. M/S Envirotech.

A-271, Okhala Industrial Area Phase-I

New Delhi - 110020

ANNEXURE 1
SAMPLE PREPARATION AND ELMENTAL ANALYSIS

a) INTRODUCTION

The chemical nature of the isotopes of an element whether they are radioactive or stable is same. Since the levels of radioactivity due to individual radionuclides in the environmental samples around NPP is too low to detect and estimate them. In order to study their behaviour in environment it would be of relevance to evaluate concentration of their stable counter parts. There are several analytical techniques which may be applied to estimate elemental concentrations in different environmental samples. The most common technique in use is atomic absorption spectrometry.

b) ATOMIC ABSORPTION AND EMISSION MEASUREMENTS

Atomic absorption and emission spectrometry deal with the absorption and emission of radiation by atoms of an element. The measurement of the energy absorbed constitutes the atomic absorption technique while the emission of radiation by the previously excited atoms or ions constitutes optical emission spectrometry. In the case of alkali metals, even a normal flame may serve as an excitation source whereas in the case of refractory oxide forming metals, high temperature plasma serves as the excitation source. The measurement of the emitted radiation using a suitable dispersing medium like gratings constitute the emission spectrometry while the measurement of masses of ions produced forms the basis of ICPMS (inductively coupled plasma mass spectrometry). All these spectrochemical techniques are valuable in environmental applications.

The absorption of radiation causes the excitation of metal atoms present in the ground state. These atoms are produced through the use of a suitable flame like air-acetylene or nitrous oxide – acetylene in the case of atomic absorption spectrometry. The atoms can also be produced by other processes like electrothermal atomisation or by the use of DC arc or inductively coupled plasma source. The processes taking place in a typical AAS experiment can be described as the introduction of the metal salt solution into the flame followed by the evaporation of the solvent, desolvation of the metal ion and the formation of free atoms. These atoms can absorb the characteristic radiation from a hollow cathode lamp and get raised to a higher excited energy state. In emission techniques, the plasma or even flame itself serves as the excitation source. The excited atoms will return to the

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ground state by the emission of radiation as they de-excite from the higher energetic level to the lower energetic levels. The measurement of this radiation enables a very sensitive mode of measurement of the concentration of an element. This forms the principle of flame or plasma emission spectrometry. In the case of normal air-acetylene flame, only very few elements like alkali metals are sensitive. Since increasing the temperature can increase the probability of emission, nitrous oxide – acetylene flame is often employed for emission measurements. In the case of plasma sources, a much higher temperature of 6000 to 10000 K is obtained and hence even refractory oxide forming elements can be converted to their excited state atoms or ions. The measurement of emission lines from excited atoms or ions forms the principle of optical emission spectrometry. Since a large number of emission lines are obtained in view of the higher energies of argon plasma sources, a very good dispersing device is needed for the resolution of the spectral lines.

c) INSTRUMENTATION

An AAS unit consists of a source of radiation, atomiser, monochromator and a detector. The components and their general layout are similar to those in the case of a spectrophotometer except that the monochromator is kept after the sample in the case of an AAS instrument.

A hollow cathode lamp serves as the source of radiation in an AAS instrument. It consists of an anode and a hollow cylindrical cathode, which is either made of the metal to be analysed or is coated with that element. The radiation emerging out of the hollow cathode lamp of a particular metal is of the exact wavelength as is necessary for the resonance absorption by the atoms of that element in the flame. Hence, considerable specificity is obtained since other elements present in the flame do not absorb the radiation. The sample is introduced into the flame through a suitable nebuliser. The sensitivity of the AAS method depends on the nebulisation efficiency and the residence time of the atoms in the light path. Since the residence time is about 10^{-3} s while nebulisation efficiency is about 5 to 10 per cent, efforts were made to improve the efficiency of nebulisation as also increase the residence time. This led to the development of flameless sources like electro-thermal atomiser. The measurement of radiation intensity is carried out using a photomultiplier as in the case of a spectrophotometer. A monochromator is used before the detector in order to filter out unwanted radiation such as those coming from the filler gas in the hollow cathode lamp, emissions from the flame, other emission lines from the source etc.

d) ELECTROTHERMAL AAS

 There are many applications where the sensitivity offered by flame AAS is insufficient as in the case of direct analysis of environmental pollutants in water and biological materials. In such cases, the sensitivity of AAS can be enhanced by the use of electrothermal atomisation technique. Electrothermal atomisers are generally a type of mini furnace (graphite furnace) in which a drop of the sample is dried and decomposed at a high temperature to produce an atomic vapour cloud. Electrothermal atomisers have conversion efficiency approaching 100% so that the absolute detection efficiencies are often 100 to 1000 times that of flame AAS. The longer residence time of the atomic vapour also contribute to the increased sensitivity of the technique. However, the technique is not cost effective since the instrument as well as the consumable is expensive. Moreover, the transient nature of the signal and the presence of gases from the sample atmosphere requires an efficient background correction mandatory. In view of the smaller sample volumes employed, typically about 10 μL, the precision of the measurement is also poor. Thus a flame AAS is preferred when the analyte concentrations are higher while ETAAS instrument is of use when the concentration levels are in the range of ng/mL.

Although flame AAS technique enjoys considerable freedom from spectral interference, there are instances of interference of physical or chemical nature. The physical interference arises when the samples and standards are different in their viscosity, for instance, water and biological fluids like blood or serum. Chemical interference occurs when stable chemical compounds are formed in the flame. An example is the interference of sulphate or phosphate in the estimation of calcium, where the formation of stable calcium sulphate or phosphate degrades the sensitivity for determination. The use of releasing agents like EDTA or lanthanide ions minimises this type of interference. Spectral interference arises when the matrix elements absorb almost at the same wavelength as the analytes. In such cases the use of an efficient background correction system is advantageous. These effects are more in the case of ETAAS and hence the use of a good background correction system is mandatory in those cases.

e) HYDRIDE / VAPOUR GENERATION AAS

Flame AAS has a poor sensitivity in the case of certain environmentally important elements such as As, Se, Te, Hg, Sb etc. In these cases, the sensitivity can be enhanced

by the use of vapour generation technique. In the case of mercury, it is possible to reduce the inorganic mercury ion to elemental mercury by the use of a suitable reducing agent like stannous chloride. The elemental mercury has an appreciable vapour pressure at room temperature and is carried through a stream of nitrogen into the optic path in a glass tube fitted with quartz windows to allow the radiation from a mercury discharge lamp to pass through. The mercury vapour absorbs the emission line of mercury from the mercury discharge lamp just as atomic mercury does in a flame. This allows a sensitive technique for the estimation of mercury in a wide variety of samples.

A similar technique is employed for the analysis of hydride forming elements like arsenic, selenium, tellurium, antimony etc. In a typical case, for the determination of arsenic in environmental samples, arsenic is generated using sodium borohydride as a reducing agent. The generated arsine is swept through a quartz tube positioned in the flame of an air-acetylene burner and aligned in such a way as to allow the radiation from the arsenic hollow cathode lamp to pass through. Arsenic atoms are produced by the dissociation of arsenic at the flame temperature and absorb radiation from the arsenic hollow cathode lamp. This results in a sensitive method for the estimation of arsenic. Detection limits in the range of 1-2 ng/ml are attainable using this technique. Commercial AAS units provide a hydride generation accessory for this purpose.

f) QUANTITATIVE CALCULATIONS FROM ABSORPTION MEASUREMENTS

The amount of monochromatic radiation absorbed by a sample is described by the Beer – Bouguer – Lambert Law, commonly referred to as Beer's law. It can be expressed mathematically as

$A = - \log T = \log (P_o/P) = a\, b\, c$

Where A is the absorbance,

T is the transmittance, representing the fraction of radiant energy transmitted and is given y P/P_o where P and P_o are the power of transmitted and original radiation respectively

a = the absorptivity and is dependent on the wavelength and the nature of the absorbing species

b = path-length, generally in cm

c = concentration of the analyte in g/l

The product of the absorptivity and the molecular weight is called the molar absorptivity. Thus $A = \varepsilon\, b\, C$ where C is expressed in moles per litre.

g) SAMPLE PREPARATION FOR AAS TECHNIQUE

The samples for elemental analysis are required to be processed and brought in a particular form before their analyses.

WATER SAMPLE

FRESH WATER SAMPLE

Since the elemental concentrations are low, large volume of the samples are required to be processed either by reducing the volume by evaporation or may be pre-concentrated using suitable reagent like MIBK.

Procedure:

1. Collect the 15 liter water sample from the desired location in a clean plastic container.

2. Filter out a known volume of sample through Whatman ni 41 and acidified with HNO_3 (3ml/l) and evaporate to near dryness.

3. Alternatively the filtered and acidified is stirred for two hours with MIBK (5mg/l). Allow the residue to settle overnight.

4. Dissolve the residue form step 2 OR step 3 in 4N HNO_3 and evaporate to dryness cool the mass and re-dissolve in 1N HCl. Make known volume of 25 ml in a standard flask.

5. Take an aliquot of sample and subject to a Beer – Bouguer – Lambert Law calibrated AAS for analysis.

6. Calculate the concentration of analysed element per liter accounting all the dilutions during the process.

SEA WATER SAMPLE

The elemental concentrations are low, large volume of the samples are required to be processed. Since the salt contents in sea water is quite high, pre-concentrated or extraction method is required to be adopted. An alternative method for estimation of trace elements in sea water is given below;

Preparation of Complexant: A 3.5% salt solution is made up by dissolving 8.75 g NaCl in 250 ml DDwater.Five grams each of APDC (ammonium pyrolidine dithiocarbamate) and DDDC (diethyl ammoniumdiethldithiocarbamate) are weghed and dissolved in the salt solution. The complxant is filtered through a Whatman No.1 paper under vacuum to remove any undissolved salts or precipitating metal containing colloids, and then stripped

of trace metals by shaking for five minutes with Methyle isobutyl ketone (MIBK) in a separating funnel. The complxant may then be stored in refrigerator.

Method of Trace Element Extraction

Take 250 to 300 ml sea water in dry and clean separating funnel of 500 ml capacity. Add appropriate ammonia to adjust pH as 7. Add 5 ml of MIBK followed by addition of 3 ml of complexant and shake for extraction of trace element into MIBK. Allow the phase to separate and isolate the organic phase in smaller separating funnel. Repeat the extraction thrice and combine the total organic layers for back extraction in the aqueous phase.

Add 5 to 20 ml DDwater and wash the organic layer. Add 2 ml distilled nitric acid followed by 5 ml double distilled water for back extraction. Repeat the extraction thrice and combine the aqueous layers. Evaporate the contents gently. Cool and transfer the contents with 0.1N HCl in a 10 ml volumetric flask and make up the volume for carrying out trace element analysis using a calibrated AAS.

WATER SAMPLE

Since the elemental concentrations are low, large volume of the samples are required to be processed either by reducing the volume by evaporation or may be pre-concentrated using suitable reagent like RKBK. The later is useful in case of sea water samples.

Procedure:

1. Collect the 15 liter water sample from the desired location in a clean plastic container.

2. Filter out a known volume of sample through Whatman ni 41 and acidified with HNO_3 (3ml/l) and evaporate to near dryness.

3. Alternatively the filtered and acidified is stirred for two hours with RMBK (5mg/l). Allow the residue to settle overnight.

4. Dissolve the residue form step 2 OR step 3 in 4N HNO_3 and evaporate to dryness cool the mass and re-dissolve in 1N HCl. Make up a known volume of 25 ml in a standard flask.

5. Take an aliquot of sample and subject to a Beer – Bouguer – Lambert Law calibrated AAS for analysis.

6. Calculate the concentration of analysed element per liter accounting all the dilutions during the process.

BIOLOGICAL SAMPLES

1. Collect the sample from the desired location in a clean plastic bag.

2. The sample is cleaned washed and dried and ashed as explained in previous sections of this document. To ash the sample either dry ashing in a silica dish using a furnace or wet ash using nitric acid and hydrogen peroxide may be chosen. The wet ash is preferred in case of samples associated with volatile elements. The smaller fishes and biota like phytoplanktons or zooplanktons are also preferred for wet ash (for wet ash known mass about 2-5 g fresh weight may be taken).

3. Take a known weight of ash (about 1 g) in a platinum crucible and dissolve in $HCLO_4$, Conc. HNO_3 & HF (2ml each) and evaporate gently to dryness cool the mass and repeat this step twice.

4. Dissolve the mass in 1N HCl. Make up a known volume of 25 ml in a standard flask.

5. Take an aliquot of sample and subject to a AAS for analysis.

6. Calculate the concentration of analysed element per gram accounting all the weights during the process.