TRAINING OF TRAINERS PROGRAMME ON CAPACITY DEVELOPMENT OF ETP OPERATORS

Promotion of Sustainability in the Textile and Garment Industry in Asia - FABRIC

giz Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH

FABRIC Asia

Day 4: Presentation 4

Effluent sampling & Analysis

Contents

- Basic aspects of sampling
- Sampling procedures & methods
- Basic principles of analysis
- Analysis procedures of important parameters

Basic aspects of sampling

Basic aspects of sampling

Important!

- ETP only functioning if correctly **monitored and controlled**

Necessary precautionary measures

- ✓ Ensure **representativeness** of sample
- ✓ Prevent **sample contamination**
- ✓ Properly **preserve, transport and store** samples
- ✓ Take **safety precautions** while taking samples

Basic aspects of sampling

Role and responsibilities

- Monitoring generally job of ETP manager and lab chemist
- Crucial role of **correct data collection & monitoring** belongs to **operator**
- correct sampling of wastewater as per set procedure!
- Without correct and representative sample wrong data and misguided control of ETP operation

Basic aspects of sampling

Main common requirements for all sampling

- **Quantity**
  - Sample to be sufficient to perform all required analytical testing
- **Quality**
  - Strictly as per sampling and handling procedures
  - Integrity of sample by avoiding sample deterioration or contamination
- **Relativity**
  - Sample to be truly representation of source

Basic aspects of sampling

Importance of ensuring occupational health & safety during sampling

- Right **safety equipment needed and provided**
- Preventive measures implemented
- Being prepared for emergency and capable of providing assistance
- Appropriate type of **personal protective equipment (PPE)** used as per requirements

QUIZ

Name the requirements of good sampling ?

Basic aspects of sampling

Six pre-requisites for quality data

- Formulating objectives and plan of sampling program
- Collecting representative samples
- Proper handling and preservation of samples
- Ensuring proper chain-of-custody & sample ID procedures
- Application of field quality assurance
- Timely and proper analysis

Sampling procedures and methods

Image: fibre2fashion

Sampling procedures & methods

Different sample collection devices and methods:

- **Automatic samplers**
  - Collecting samples by periodically pumping a sample into sample bottle/s.
  - Triggered to sample by a set time or amount of liquid passing by flow-measuring device.
- **Using sample dip-poles**
  - Expandable plastic or aluminum rods (upto 20ft) with special device securely holding sample botte at end
- Dipping sample bottles for **manual sampling**

Sampling procedures & methods

Grab composite sample

Useful for parameters like total oil and grease released to sewer system in 24-hours period

Step 1:

- Grab individual samples in field and composite on site or in laboratory

Step 2:

- Record flow level at time of each sampling (for flow-proportional grab composite)

Step 3:

- Make composite sample with portions of each grab sample according to each flow level at time of sampling

Sampling procedures & methods

Discrete sampling

- Used when looking at specific characteristics of wastewater flow
  - ✓ At **certain times** of day
  - ✓ For **certain parameters** (e.g. high or low pH; high or low flow events)
  - ✓ For **flow composites** (if flow rate recorded at time of sampling)
- **Recommended procedure**:
  - ✓ samples are taken in individual bottles at the time of the event and each sample is analyzed

Sampling procedures & methods

To remember when sampling for Volatile organic compounds

- Collect samples in clean glass beaker
- Transfer samples to 40 ml vials (usually with HCl acid for preservation) and cap with flexible septum
- Prevent air bubbles in vial (with no air space under cap)
- filling vial filled until liquid crowning.
- Tightly screwing cap until bulging septum

Sampling procedures & methods

To remember when sampling for heavy metals

- Be aware of **contamination** during sampling
- **Avoid metal** (including stainless steel) **sampling equipment -** Use plastic sampling equipment where possible.
- Use of deionized instead of distilled water for decontamination to Prevent effects from **trace metals**

Sampling procedures & methods

To remember when sampling microbiological analytes

- Large sample volumes required being easily contaminated by bacteria present on most surfaces and in air
- Maintain **short holding times** (preferably less than 6 hours)
- **Wash and disinfect hands** with alcohol based hand disinfectant prior to and between sample collection
- **Wear and change latex gloves** between samples to avoid contamination of samples during collection
- **Directly collect samples** into sample container whenever possible

Sampling procedures & methods

Moveable samplers
(model RS Hydro)

Automatic sampling types

- **Time-controlled water and wastewater sampling**
  - ✓ Enter desired time interval and sample volume in menu and allow sampler to operate
  - ✓ Some water samplers equipped with cooling of composite samples
- **Flow-proportional water and wastewater sampling**
  - ✓ Equipped with a transmitter that is able to receive external signals (e.g. from a flowmeter)
  - ✓ Sampling can be adapted to the flow rate

Sampling procedures & methods

Stationary samplers (model Endress & Hauser)

Automatic sampling types

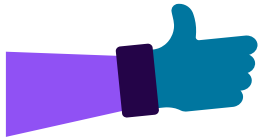
- **Event-triggered water and wastewater sampling**
  - ✓ Able to detect high loads of wastewater and trigger sampling automatically with analytical sensors
  - ✓ Providing reliable evidence about peak loads in effluent flow and making representative sample
  - ✓ Mostly used in inlet of wastewater treatment plants with irregular wastewater flows

QUIZ

Name the advantage & disadvantage of automatic sampling?

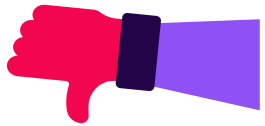
Sampling procedures & methods

Automatic sampling - Pros & Cons



Advantages

- Convenient (no need for work during night/weekends)
- Safe (no need to stay at unsafe locations for long time)
- Able to record and analyze data from off-site locations
- Automatically recording of data on sampling like time, quality of samples



Disadvantages

- High equipment costs
- Prone to failure (need of care to maintain and to charge batteries)
- High protection of equipment and good maintenance needed

Sampling procedures & methods

Manual sampling - Procedure

- **Wear** new clean, **non-powdered, disposable gloves** for each sample
- Change gloves any time during sample collection if coming in contact with sampled effluent
- **Avoid contacting media** being sampled.
- Proceed with sampling from least to most suspected contaminated area
- Samples from highly contaminated media to be placed in ice chest
- Sample as a team (of at least two persons -one collecting samples, one taking notes, photographs and fill out tags)

Sampling procedures & methods

Collecting time composite manual sampling

- Discrete sample aliquots of equal volume collected at constant time intervals in container
- Example: 100 ml sample every hour to form 800 ml sample for an 8 hour shift.
- Collection of **constant sample volume at varying t**ime intervals proportional to wastewater flow
- Collection by **varying vol**ume of each aliquot **proportional to flow** while maintaining **constant time** interval between the samples.

Good practices in handling samples

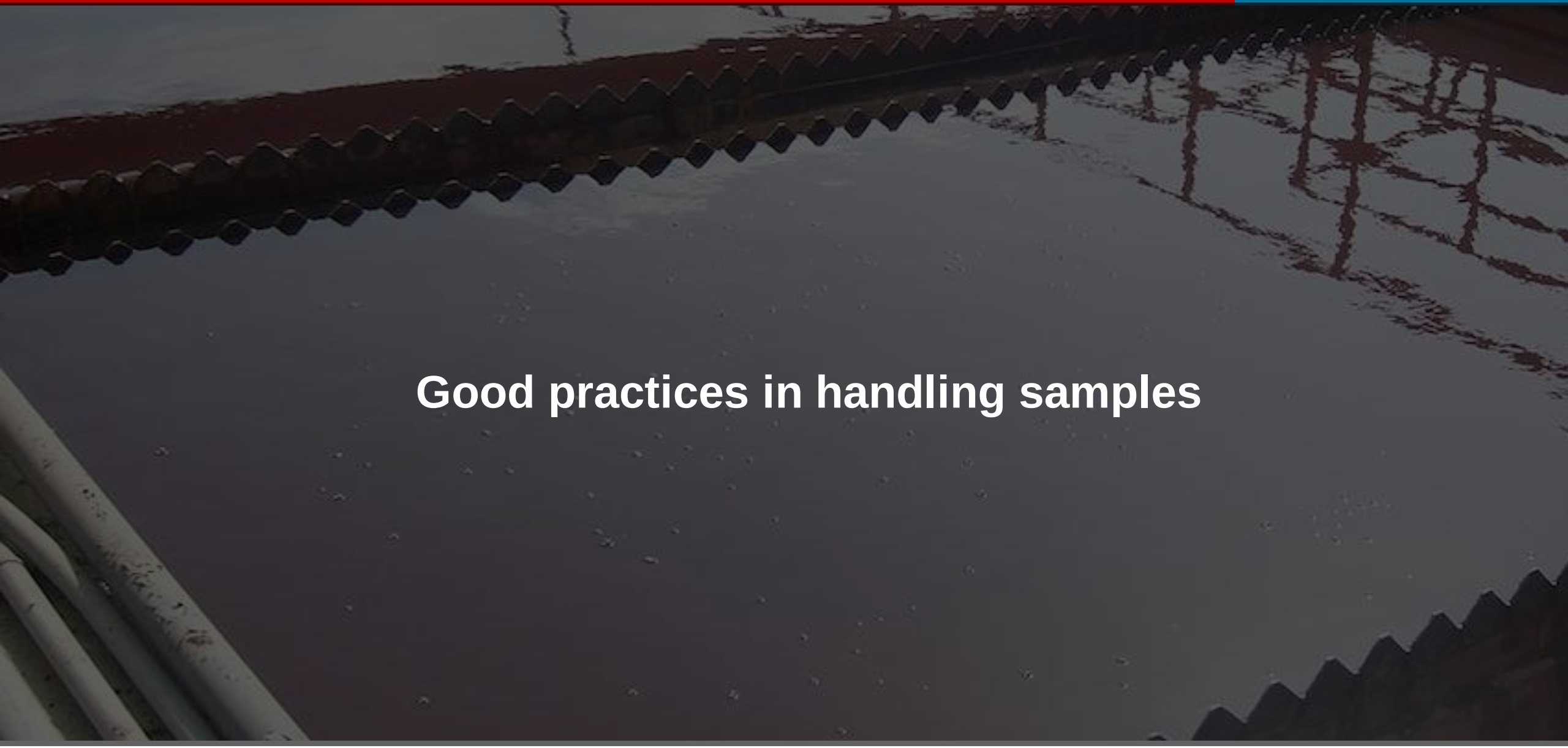


Image: fibre2fashion

Good practices in handling samples

Good practices in selecting sampling locations

- **Raw effluent samples**
  - ✓ Take sampling at **inlet of screens**
  - ✓ Avoid scraping bottom and stirring up sediments with sampling cup
- **Equalized effluent samples**
  - ✓ Take sample at **outlet of equalization tank transfer pump** effluent falling into flash mixer/neutralization
  - ✓ Better to take and mix **4 - 6 samples** from **different points from inside of tank**

Good practices in handling samples

Good practices in selecting sampling locations

- **Primary, tertiary and final treated effluent**
  - ✓ Take sample at overflow from respective settling tank
  - ✓ Avoid taking samples from overflow launder
- **MLSS**
  - ✓ Take samples at inlet of secondary clarifier or overflow weir of aeration tank

Good practices in handling samples

Good practices in selecting sampling locations

- **Avoid contact** of collecting device contact **with sample containers** when transferring samples
- Place samples into **appropriately labeled containers**
- **Store samples** for volatile organic compounds and BOD analysis **without any headspace**
- Immediately **place samples on ice** Samples requiring reduced temperature storage.
- Preserve samples as soon as practically possible

Good practices in handling samples

Labelling of samples

- Clear **sample identification at all times** essential
- Recommended contents of label
  - ✓ To recorded in **Field Record Sheet**
  - ✓ Retained as **permanent record**

- Date of sampling
- Time of sampling
- Location and name of sampling site (GPS coordinates)
- Job or project number
- Name of sampler
- Container pre-treatment and preservations added
- Other observations affecting method or results of analysis

Good practices in handling samples

Sample chain of custody

- To **demonstrate sample control** giving confidence about sample integrity
- Imperative if samples
  - ✓ to be **used in legal proceedings**; or
  - ✓ any suspicion of tampering samples at any stage of process.
- Records for **tracing sample possession and handling** from collection, analysis, reporting to disposal
- Use for **protection of sample couriers** assume responsibility for container and not content
  - ✓ sample to be secured with adhesive tape to prevent tampering by courier.

Good practices in handling samples

Sample transport and storage

To maintain **quality and reliability of analysis** results

- Pack properly to avoid breakage and cross-contamination
- Appropriate preservation to reduce sample degradation
- Not to exceed holding time between sampling and analysis
- Sample containers sealed, carefully packed with suitable packing material
- Sample chilled or frozen (as required) and transported in appropriate cooler or fridge

QUIZ

What is a legal sample?

Good practices in handling samples

Legal sampling for use in penal action and legal cases

- Taken by authorized persons from enforcement agency (e.g. DOE)
  - ✓ Person taking sample to serve **notice to factory management**.
  - ✓ Sample to be taken in **presence of authorised person and factory representative** and divided into **two sample parts**
  - ✓ Both samples to be **marked and sealed with signatures** of factory and enforcement agency representatives
  - ✓ One sample to be sent to authorised laboratory for analysis (cost paid by factory) by factory, sealed by enforcement agency.
  - ✓ Second sample to be kept for analysis by department laboratory (e.g. DoE)

Laboratory analysis

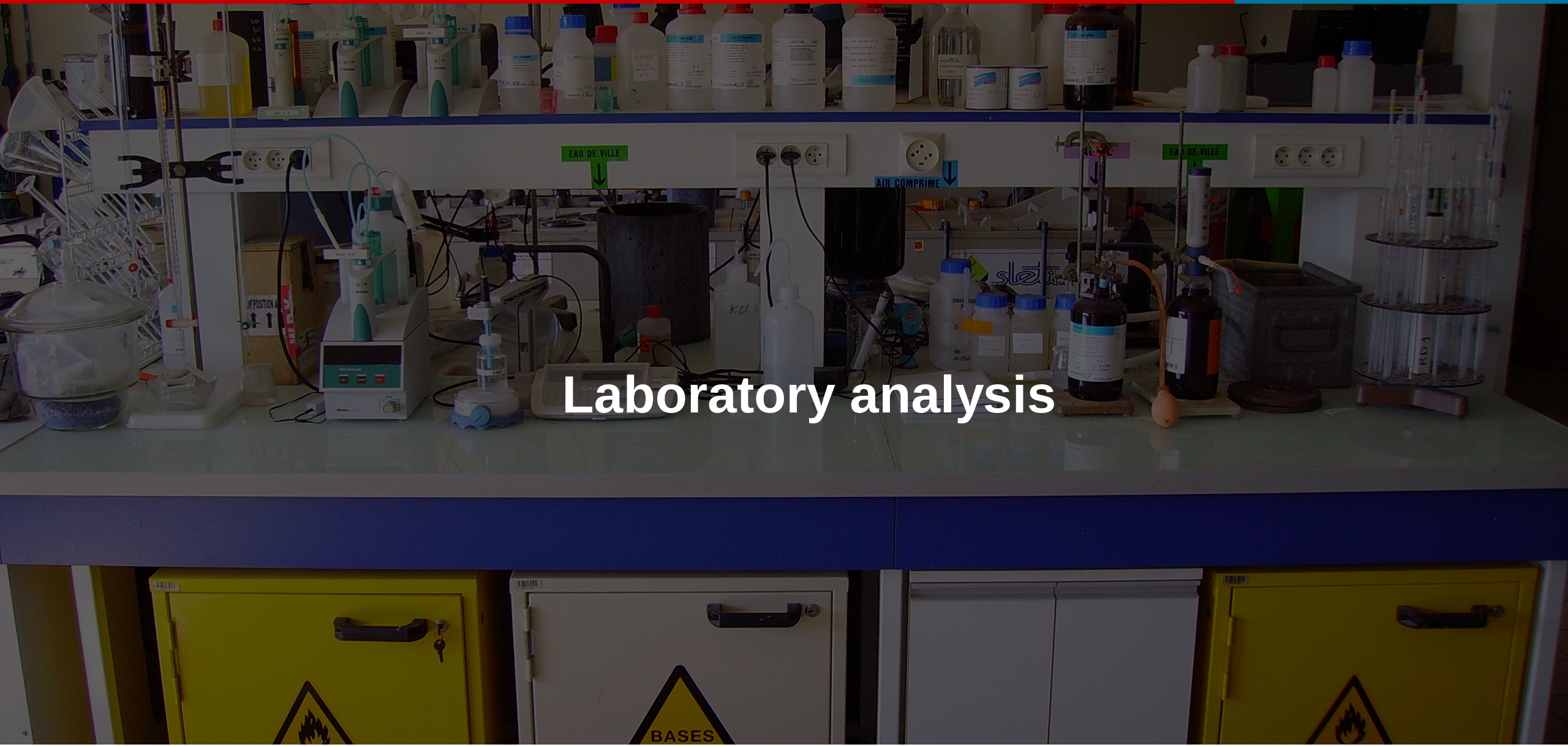


Image: fibre2fashion

Laboratory

- Yes...laboratory is territory of chemist, not operator. But It is useful if operator know basic testing methods
- Discussion is only essence of most important parameters We have included only pH, TSS, BOD, COD, TDS, alkalinity.
- MLSS is basically TSS and DO testing is part of BOD analysis.
- Colour, nitrogen, phosphorous, etc. too are relevant, but need instruments such as spectrophotometer.
- MLVSS need a muffle furnace.

Lab Safety Measures

- Know location and operation of fire extinguishers, eye wash bottles, and overhead showers.
- Be alert and cautious in handling chemicals. If acid or alkali spills on you, flush with tap water immediately.
- When heating chemicals, ensure container mouth not pointed towards anyone. Serious burns by eruption
- Wipe up any spill immediately and rinse the area several times with tap water.
- After you complete any tests, wash all glassware and clean any other apparatus used for testing.

Testing of pH

- Spot checking is done using portable pH meter or pH paper
- Counter-checking of pH done at the laboratory
- Laboratory table top pH meters are very common and inexpensive.
- They consists of the meter, combination electrode and stand for the electrode to be dipped in the sample.
- Electrodes need to be rinsed thoroughly before and after testing samples.
- Periodic calibration is very important using the calibration solution.

Testing of Suspended solids

- Weigh the filter paper and note the initial weight.
- Place filter paper in the filter holder, wet it to seat it, secure funnel to the base. If available, connect the vacuum suction.
- Filter as much effluent sample as is possible within a 10-minute span, up to 1 litre. Record the total sample volume filtered. For MLSS, smaller quantity used.
- Once it is finished, wash filter to remove dissolved solids. Continue suction for about three minutes more.

Testing of Suspended solids

- Take paper cone, place it in drying oven set at 104±1°C for at least one hour.
- Remove filters/pans from oven & place in a desiccator until it cools to room temp.
- Weigh filter paper on a balance to the nearest 0.0001 g and record the final weight.

Testing of Suspended solids

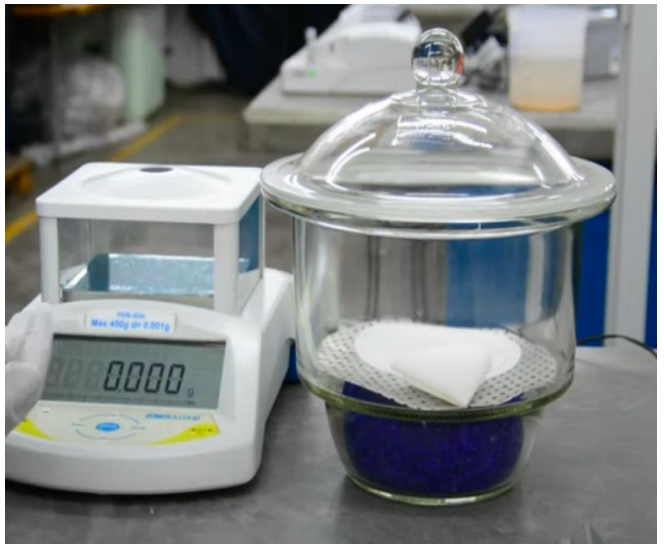
TSS in the effluent, mg/l =

$$\frac{\text{Final weight of the filter paper (mg)} - \text{Initial weight of filter paper (mg)} \times 1000}{\textbf{Sample Volume in (ml)}}$$

Testing of Suspended solids

Filter the effluent through filter paper cone

Dry it in the oven @ 104°C for minimum one hour



Dry it in the desiccator & then take final weight in a electronic balance.

Testing of Dissolve solids

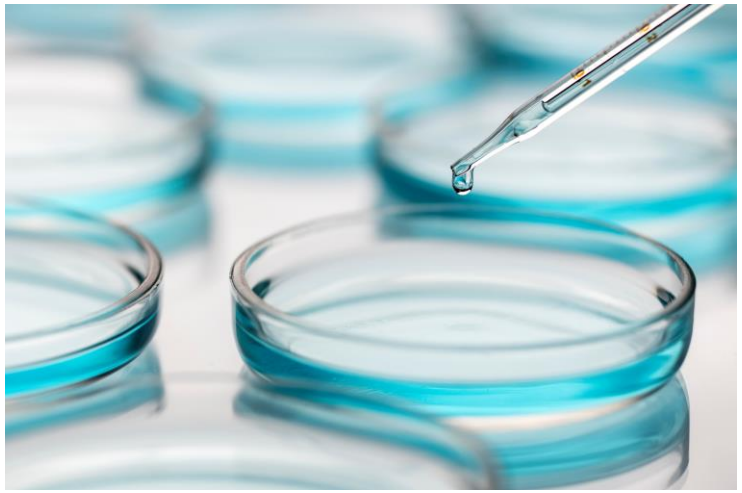
1. Easy way to check total dissolved solids is a TDS meter. But measurement of TDS by gravimetric method in laboratory is more accurate, as follows:
2. Place a filter paper in the filter holder. Filter a known quantity of wastewater to **remove all suspended solids**.
3. Weigh a dry evaporating dish (crucible) to note the **initial weight**. Transfer a known quantity of filtrate to to it
4. Evaporate to dryness on a steam bath or in a drying oven.
5. Dry evaporated sample for at least 1 h in an oven at 180 ^{o} $\pm$ 2°C, cool in a desiccator to room temperature, and weigh evaporating dish as final weight.

Testing of Dissolve solids

TSS in the effluent, mg/l =

$$\frac{\text{Final weight of the Crucible (mg)} - \text{Initial weight of Crucible (mg)}}{\text{Sample Volume in (ml)}} \times 1000$$

Preparation for dissolved oxygen testing



- Where possible sample should be collected in a 300 ml bottle with flared opening and ground glass stopper.
- Precautions to avoid air entrainment and dissolution of atmospheric oxygen.
- Insert stopper by letting the stopper slip into opening and ensure that no air bubbles exist in the bottle.
- Sample temperature should be noted.
- Dissolved oxygen determination initiated immediately.
- The sample may be fixed in field for preservation for up to 4 to 8 hours before the final analysis is completed.

Testing of Dissolve oxygen

- Dissolved oxygen (DO) is a primary indicator of pollution of a water.
- It is vital parameter for survival of fish etc. in receiving water.
- It is one of discharge standards stipulated by DoE. DO testing is important in controlling aeration tank operation.
- DO determination relies on oxidizing power of oxygen done either by DO meter or standard Winkler method in lab.
- Now most DO determinations are made with DO meters.

Testing of Dissolve oxygen

Stage 1:

- Take sample in the bottle.
- Add Manganese sulphate
- Add Alkali Iodide-Azide

This will precipitate manganese hydroxide. Qty of precipitate is proportional to the free oxygen in the sample.

Testing of Dissolve oxygen

Stage 2:

- Add Concentrated sulphuric acid.
- Shake the bottle well

This will dissolve the precipitate and generate free Iodine proportional to the dissolved oxygen in the solution.

Testing of Dissolve oxygen

Stage 3:

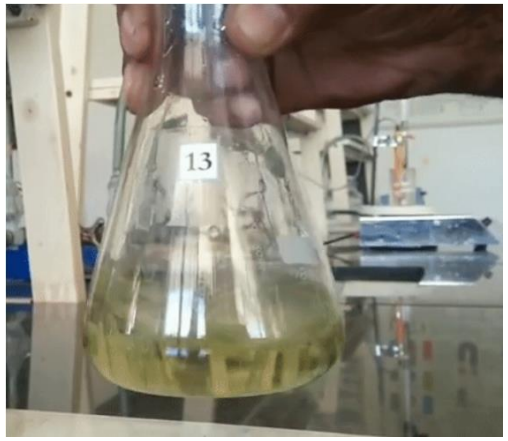
- Find the free iodine by addition of sodium thiosulphate (0.25 N).
- Free iodine is consumed by thiosulphate.
- Add starch as an indicator towards end to give blue colour.
- Once iodine is fully consumed, the solution becomes colour less.

Testing of Dissolve oxygen

Dissolved oxygen in the effluent, mg/l =

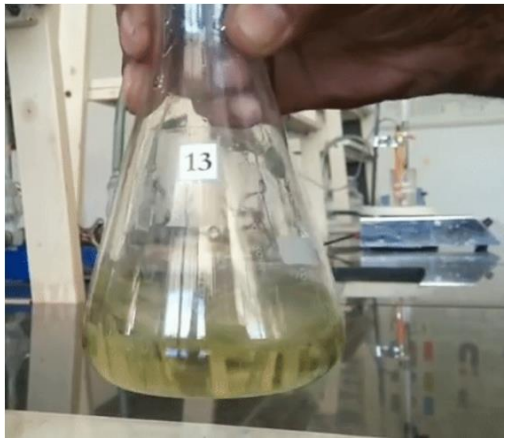
$$\frac{\text{Volume of sodium thio-sulphate (ml)} \times \text{Normality of thio (0.25)} \times \text{Eq. Wt of oxygen (32)} \times 1000}{\text{Sample Volume in (ml)}}$$

Testing of COD



- Chemical oxygen demand is measure of **compounds oxidized chemically**.
- Principle is to oxidise solution using potassium dichromate and remaining dichromate is found through titration with ferrous ammonium sulphate. Dichromate consumed is proportional to COD of sample.
- Results can usually be obtained in 2½ hours. All samples (especially if TSS is high) should be well mixed.
- Biologically active samples should be tested as soon as possible. May be preserved for short periods by refrigeration to temperatures below 5°C.
- Preservation technique for upto a week is to add 2 mL of concentrated sulphuric acid per one liter of sample.

Testing of COD



- **Potassium dichromate** (0.25 N) is oxidant. Concentrated sulfuric acid, is added to achieve acid conditions and heated.
- Pinch of silver sulfate is added as a catalyst to oxidize complex organics, pinch of mercuric sulphate for chloride interference.
- Sample is refluxed (boiled without loss of vapor) with known **dichromate** and other reagents until oxidation is completed. Run a **blank** too distill water.
- The excess dichromate remaining after refluxing is titrated with standard **ferrous ammonium sulfate** (FAS) of 0.1 N, solution.
- The indicator used is ferroin which complexes with the first appearance of excess Fe2+ at the end of the titration to give a sharp color change.

Testing of COD

Before Digestion

Following Digestion

Immediately before titration end-point

Immediately after titration end-point

Testing of COD

COD in the effluent, mg/l =

$$\frac{\text{Volume of Ferrous Ammonium sulphate for Blank (ml)} - \text{Volume of Ferrous Ammonium sulphate for Sample (ml)} \times \text{Normality of FAS used (0.1)} \times 8000}{\text{Sample Volume in (ml)}}$$

Testing of COD

- Biochemical oxygen demand (BOD) test is used for determining quantity of biodegradable organics. It is used to decide if biological treatment is feasible
- BOD value in effluent indicate how much oxygen effluent will consume if it is discharged into a water body.
- The determination of BOD should not be delayed. If the determination cannot be done immediately, holding sample at 4°C is required until the test is begun.
- The maximum time delay from sample collection to analysis is 6 hours.
- If sample requires the addition of seed, the seed must be ready before test.

BOD incubator & BOD bottles

Testing of COD

- To determine BOD, known dilution of sample (dilute it more if the BOD value is likely to be high) in a **300 ml BOD bottle**. Fill it with aerated water,
- Keep a **blank** (without sample). Check the initial DO.
- Add a small amount of seed in all bottles, cap it and keep it incubated for 5 **days in a BOD incubator kept at 20^{O}C**.
- If no BOD incubator, rough measurement can be done at 27^{O}C for 3 days.
- On 5th day, check DO in all samples calculate BOD from equation provided.

Testing of COD

BOD in the effluent, mg/l =

$$\frac{\left(\text{DO in the sample first day, mg/l} - \text{DO in the sample 5th day, mg/l}\right) - \left(\text{DO in the Blank first day, mg/l} - \text{DO in the Blank 5th day, mg/l}\right)}{\text{Sample Volume in (ml) taken in the BOD bottle} \div \text{Volume of BOD bottle (300 ml)}}$$

To conclude

- For proper analysis result, sampling & analysis of wastewater be proper.
- Grab sampling & composite sampling are usual mode of sampling: should be selected based on location of sampling & parameters to be tested.
- Knowing testing of pH, COD, DO and MLSS (TSS in aeration tank), operator can control the ETP process quite effectively.

To conclude

- A mini laboratory set up in ETP itself, complete with spot testing arrangement a very useful tool in ETP management.
- For full analysis procedures, study ‘Standard Methods for examination of Water & Wastewater’ published by APHA & others.

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