TRAINING PROGRAMME FOR ETP OPERATORS IN TEXTILE INDUSTRY

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

giz Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH

FABRIC Asia

Analysis of wastewater

GIZ FABRIC – ETP Operator Course

Contents

- Basic aspects of wastewater analysis
- Introduction to common wastewater tests

Basic aspects of wastewater analysis

Basic aspects of wastewater analysis

Role and contribution of operator

- Usually primary **responsibility of chemist** or **ETP manager**
- Good to know basic testing methods and principles since strong role of operators in sampling

Basic aspects of wastewater analysis

Overview of key wastewater laboratory tests

Basic testing methods:

- pH
- Total Suspended Solids (TSS)
- Biological Oxygen Demand (BOD)
- Chemical Oxygen Demand (COD)
- Total Dissolved Solids (TDS)
- Alkalinity

Basic aspects of wastewater analysis

Overview of key wastewater laboratory tests

- **Other** testing methods (selected):
  - Colour
  - Nitrogen
  - Phosphorous
  - Mixed liquor volatile suspended solids (MLVSS)
    - tested with muffle furnace.

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Basic aspects of wastewater analysis

Basic laboratory rules

Attention to **locations and operations**

- Familiarize with fire extinguishers, eye wash bottles, and overhead showers.
- Avoid serious burns boiling chemicals while heating: Do not point container mouth towards yourself or anyone nearby!

Attention to **cleanliness** of laboratory

- If acid or alkali spills on you, immediately flush body area with tap water!
- Immediately clean any spill and rinse area several times with tap water!

To-do **after completion of test**

- Wash all glassware and clean any other apparatus used for testing.

Introduction to common wastewater tests

Introduction to common wastewater tests

1. Testing of pH

- Using laboratory **table top pH meters**
  - very common and inexpensive
  - consisting metering device, combination electrode and stand for electrode to be dipped into sample
- Good practices
  - Electrodes to be rinsed thoroughly before and after testing samples
  - **Periodic calibration** very important using calibration solution

Introduction to common wastewater tests

2. Testing of Total Suspended Solids (TSS)

Procedure

(1) **Weigh filter paper** and note its initial weight

(2) Place filter paper in filter holder and **wet with small amount of distilled water** to seat it

(3) Secure funnel to base. If available, connect vacuum suction.

(4) **Filter** as much **effluent sample** as possible (up to 1 litre) within a **10-minute span**

(5) Record total sample volume filtered

- for MLSS, filter smaller quantities

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2. Testing of Total Suspended Solids (TSS)

Procedure (contd.)

6) Wash filter with distilled water to remove any dissolved solids.
7) Continue suction for about three more minutes
8) Take **paper cone** and place **in drying oven** set at 104±1°C for at least one hour.
9) Remove **filters/pans** from oven and place **in desiccator** until it cools to room temperature
10) Weigh filter paper on fine-balance to nearest 0.0001 g and record **final weight**

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2. Testing of total suspended solids

Determining the TSS in the effluent, mg/l =

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

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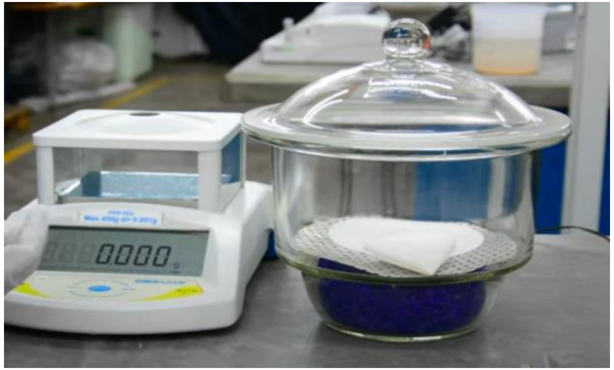
2. Testing of Total Suspended Solids (TSS

Filter the effluent through filter paper cone

Dry it in the oven @ 104ºC for minimum one hour



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

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3. Testing of total dissolved solids

Gravimetric procedure (als Alternative zu TDS Meter)

1) Place filter paper in filter holder.
2) Filter known quantity of wastewater to remove all suspended solids
3) Weigh dry **evaporating dish** (crucible) to note **initial weight**
4) Transfer known quantity of filtrate to evaporation dish
5) Evaporate to dryness on steam bath or in drying oven.
6) Dry evaporated sample for at least 1 hour in oven at 180 º $\underline{+}$ 2°C, let cool in desiccator to room temperature, and **weigh evaporating dish as final weight**

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3. Testing of total dissolved solids

Determining TDS in the effluent, mg/l =

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

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3. Testing of total dissolved solids

Filter the effluent through filter paper cone

Transfer the filtrate to a evaporation dish (crucible)

Dry it in a water batch to maximum dryness

Dry it in the oven @ 180^{o}C $\pm$ 2 ^{o}C for minimum one hour

Dry it in the desiccator

take final weight in a electronic balance.

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4. Testing of dissolved oxygen (DO)

Primary indicator for **pollution state of water** and vital parameter for survival of fish etc. in receiving water.

- One of discharge standards **stipulated by DoE**
- DO measurement most important in **controlling aeration tank operation**
- Method relying on oxidizing power of oxygen and done by
  - **DO meter**
  - standard **Winkler method** in laboratory.

Mostly used tool for DO determinations: **DO meters**

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4. Testing of dissolved oxygen

Procedure for collection and preservation

- Collect **sample in 300 ml bottle** with flared opening and ground glass stopper
- **Avoid air entrainment** and dissolution of atmospheric oxygen in bottle:
  - Insert stopper by letting it slip in and ensure **no air bubbles**
- Note **sample temperature**
- **Immediately initiate DO determination**
  - Fix sample in field for preservation for up to 4-8 hours before final analysis completion

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4. Testing of dissolved oxygen

Stage 1

- Take sample in bottle and add Manganese sulphate and Alkali Iodide-Azide
  - Precipitating manganese hydroxide
  - Quantity of precipitate proportional to free oxygen in sample

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4. Testing of dissolved oxygen

Stage 2

- Add concentrated sulphuric acid
- Shake bottle well.
  - Precipitate dissolved generating free Iodine proportional to dissolved oxygen solution.

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3. Testing of dissolved oxygen

Stage 3

- Add sodium thiosulphate (0.25 N) to find free iodine
  - Free iodine consumed by thiosulphate
- Towards end add starch as indicator to give blue colour.
  - Once iodine fully consumed, solution becoming colour less.

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4. Testing of total dissolved oxygen

Determining DO in effluent, mg/l =

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

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5. Testing of chemical oxygen demand (COD)

Measure of compounds **oxidized chemically**

Principle

- Oxidize solution using potassium dichromate.
- Find remaining dichromate through titration with ferrous ammonium sulphate
  - Dichromate **consumed proportionally to COD** in sample
- Important to mix all samples well (especially if TSS high)

Results **obtainable in 2 ½ hours** usually!

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5. Testing of chemical oxygen demand (COD)

Preservation

- Biologically active samples to be **tested as soon as possible**
  - Samples preserved for short periods by **refrigeration** to temperatures **below 5°C**.
  - For preservation up to one week add 2 mL of concentrated sulphuric acid per one liter of sample

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5. Testing of chemical oxygen demand (COD)

Procedure

(1) Use **potassium dichromate** (0.25 N) as oxidant.

(2) Add **concentrated sulfuric acid** to achieve acid conditions **and heat**

(3) Add pinch of silver sulfate as catalyst to oxidize complex organics

(4) Add pinch of mercuric sulphate for chloride interference

Before Digestion Following Digestion

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5. Testing of chemical oxygen demand (COD)

Procedure (contd.)

4) Boil sample without vapor loss (reflux) with known amount of **dichromate** + other reagents until oxidation completed

5) Run **blank** to distill water

6) Titrate excess dichromate with standard **ferrous ammonium sulfate** (FAS) of 0.1 N, solution.
   – Ferroin as indicator used being complexed with first appearance of excess Fe^{2+} at end of titration giving sharp color change.

Immediately before titration end-point | Immediately after titration end-point

5. Testing of chemical oxygen demand (COD)

Determining COD in effluent, mg/l =

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

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6. Testing for alkalinity

Indicating **capacity to neutralize acids**

- Testing normally relevant for ETPs with anaerobic treatment systems.
- **Alkalinity ions**:
  - bicarbonate & carbonate (CO_3^{2-})
  - In most effluents, alkalinity primarily caused by carbon dioxide-carbonate.

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6. Testing for alkalinity

Concept of analytical procedure

- Assumed only OH-, bicarbonate, and carbonate contributing
  - Results affected if other ions significantly present (!)
- **Total alkalinity** measuring contribution from OH-, bicarbonate, and carbonate ions
- **Phenolphthalein alkalinity (PA)** measuring contribution from carbonate and OH ions

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6. Testing for alkalinity

Concept of analytical procedure

- Alkalinity levels showing up in **different colorations** with phenolphthalein and methyl orange
- Titration of sample with acid until:
  - pH approximately 4.5; and
  - all carbonate and bicarbonate species converted to CO_2 or carbonic acid (H_2CO_3).

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6. Testing for alkalinity

Procedure

(1) Measure **phenolphthalein alkalinity** during titration to endpoint pH 8.3

- Phenolphthalein pink above a pH of 8.3 and colorless below
- **Stop titration at pH of 8.3** and **record amount of acid added**

Phenolphthalein alkalinity: At start after addition of phenolphthalein and at end point.

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6. Testing for alkalinity

Procedure

(2) Determine **total alkalinity**

- Add **methyl orange** as new indicator
- Continue titration until methyl orange changing from **yellow to pinkish orange**.

Methyl orange alkalinity: After addition of methyl orange indicator and at end point.

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7. Testing Biochemical Oxygen Demand (BOD)

- Used for determining quantity of **organics biologically degradable**
- Major parameter to decide if **feasibility of biological treatment**
- Indicating how much oxygen effluent consuming if discharged into water body

BOD incubator

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7. Testing Biochemical Oxygen Demand (BOD)

Preservation

- Determination of BOD **not be delayed**.
  - If not be done immediately, holding of **samples at 4°C** required until beginning of tests
- **Maximum time 6 hours** between sample collection to initiation of analysis
- If **seed addition**, seed to be ready at **beginning of test**

BOD bottles

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7. Testing Biochemical Oxygen Demand (BOD)

Procedure

(1) Take known dilution of **sample in 300 ml BOD bottle**

- Dilute more if BOD value likely to be high
- Fill with excess water of high DO

(2) Keep **blank** (without sample) and check dissolved oxygen

(3) Add small amount of seed in all bottles, cap and keep incubated for **5 days in BOD incubator at $20^{O}C$.**

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7. Testing Biochemical Oxygen Demand (BOD)

Procedure (contnd.)

(4) If no BOD incubator, **rough measurement** possible while keeping samples at **27^{O}C for 3 days**

(5) Check DO in all samples on day 5

(6) Calculate BOD from equation provided (see next slide)

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7. Testing Biochemical Oxygen Demand (BOD)

Determining BOD in 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 remember

- Wastewater analysis primarily job of ETP chemist or ETP manager, but **operators** as **key** persons
  - sample **collection and preservation**
  - possible support in an analysis
- **Useful to know** for operator
  - Basic idea how test results arrived at
  - Understand **results and their limitation** such as of pH, COD, DO and MLSS (TSS in aeration tank) to **effectively control ETP** processes

For further consideration

- Set-up **mini laboratory** in ETP to strengthen together spot testing capacities for
  - streamlining operational control of ETP
  - ETP performance monitoring
  - reporting to DOE and brands
- Study **‘Standard Methods for examination of Water & Wastewater’** published by APHA et al.

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