1. **Total Solids**

Principle: Total solids are determined as the residue, after evaporation of the unfiltered sample.

Procedure: An evaporating dish of suitable size is taken and weighed. 25ml of unfiltered sample is evaporated in the dish in a hot air oven. The final weight is taken after evaporation of sample.

\[
\begin{align*}
\text{Wt. of dish} & = W_1 \text{ g} \\
\text{Wt. of dish + residue} & = W_2 \text{ g}
\end{align*}
\]

\[
\therefore \text{Total Solids} = \frac{\text{Wt. of dish with residue} - \text{Wt. of dish}}{25} \times 10^6 \text{ ppm}
\]

2. **Total dissolved solids**

Principle: TDS are determined as the residue left after evaporating the filtered sample.

Procedure: An evaporating dish of suitable size is taken and weighed. 25 ml of the filtered sample is evaporated in the dish in a hot air oven. The final weight of the dish is taken after evaporation of the sample.

\[
\text{TDS} = \frac{\text{Initial wt. of the dish} - \text{Final wt. of dish}}{25} \times 10^6 \text{ ppm}
\]
Total suspended solids

Total solids and TDS are determined first and the total suspended solid is determined by the difference between TS and TDS.

\[ \text{Total suspended solids} = \text{TS} - \text{TDS} \]

\[ = \text{ppm} \]

**ESTIMATION OF TOTAL ALKALINITY**

Principle: Total alkalinity is a measure of total capacity of liquid to neutralise the strong acids. The alkalinity of the sample is generally imparted by the salts of carbonates, bicarbonates, phosphates, nitrates and silicates, together with hydrogen ion in the free state. Total alkalinity can be estimated by titrating the sample with an acid of known normality using methyl orange as indicator.

**Reagents**

1) HCl (0.1N)
2) Methyl Orange indicator

**Procedure**

20ml of sample is taken in a conical flask. Add 2 to 3 drops of phenolphthalein indicator. The pink colour developed, note the volume of HCl required. Then add 2 to 3 drops of methyl orange indicator and titration is continued till the colour changes from orange to pink. Note the volume of HCl required.
In case pink colour does not appear after the addition of phenolphthalein indicator, continue the methyl orange step.

<table>
<thead>
<tr>
<th>Vol of Sample (ml)</th>
<th>Burette reading</th>
<th>Vol of HCl (ml)</th>
<th>Concordant value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0</td>
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<tr>
<td>20</td>
<td>0</td>
<td>0</td>
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</tr>
</tbody>
</table>

Total alkalinity = \( \frac{\text{Vol. of HCl} \times \text{N. of HCl} \times 50}{20} \times 1000 \)

= \[ \text{mg/l of CaCO}_3 \]

**ESTIMATION OF DISSOLVED OXYGEN**

Principle: When manganous sulphate is added to the liquid sample followed by alkali, manganous hydroxide is formed. It is readily combined with DO and forms manganic oxyhydrate. On acidification, manganic oxyhydrate reacts with KI liberating iodine that is equivalent to oxygen present. Liberated iodine is titrated against sodium thiosulphate using starch as indicator. Endpoint is the disappearance of blue colour.

**Reagents**

i) Manganous sulphate solution
Dissolve 48g of manganous sulphate in 100ml of distilled water.

ii) Alkali iodide
Dissolve 50g NaOH or 70g KOH and 13.5g of NaI or 15g of KI in 100ml of distilled water.
iii) Sodium thiosulphate solution (0.1N)
Dissolve 24.86 g of sodium thiosulphate in 100ml of distilled water.

iv) Sodium thiosulphate solution (0.025 N)
Dilute 250 ml of 0.1N stock thiosulphate solution into 1000 ml. Preserve by adding 10ml of chloroform per litre. This solution should be titrated against standard $K_2Cr_2O_7$ solution.

v) Starch indicator
0.5g of starch powder dissolved in minimum volume of distilled water and pour it into 100ml boiled water cool and use as indicator.

Procedure

i) Completely fill a 300ml BOD bottle with the sample to be analysed by siphoning the sample slowly into the bottle and allowing it to overflow for a period to displace the volume of the bottle two or three times. Be sure that no air is entrapped.

ii) Hold the tip of the pipette below the surface of the liquid and add 1ml of manganese sulphate solution and 1ml of alkali-iodide solution.

iii) Replace the stopper, being careful not to entrap air bubbles and mix well by gentle inversion. Allow formed precipitates to settle.

iv) Remove stopper and add 1ml of conc. $H_2SO_4$ along the neck of the bottle. Hold pipette above the surface of the liquid. Replace stopper, mix by gentle inversion until no floc is visible. Allow to stand for atleast 5 minutes.

v) Withdraw 201 ml of the solution into the conical flask by use of volumetric flask and titrate with sodium thiosulphate solution until yellow colour almost disappears.

vi) Add 1ml of starch indicator and continue titration until the blue colour just disappears.
Calculation: Sample (before incubation) Vs thio

<table>
<thead>
<tr>
<th>Vol of Sample (ml)</th>
<th>Burette reading Vol.of Thio (ml)</th>
<th>Concordant value (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
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<tr>
<td>200</td>
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</tr>
</tbody>
</table>

200ml of the blank sample = X ml of 0.025 N thio

200 x Normality of oxygen in diluted blank = X x 0.025

Normality of oxygen in diluted blank = \[ \frac{X x 0.025}{200} \]

Quantity of oxygen in diluted blank = \[ \frac{X x 0.025}{200} \times 8 \text{ g/lt} \]

Since 10ml of sample is diluted to 1000 ml,

Quantity of oxygen in diluted blank = \[ \frac{X x 0.025}{200} \times 8 \times \frac{1000}{10} \text{ g/lt} \]

\[ \text{DO} = \frac{X x 0.025}{200} \times 8 \times \frac{1000}{10} \text{ g/lt} \]

Sample (after incubation) Vs thio

<table>
<thead>
<tr>
<th>Vol of Sample (ml)</th>
<th>Burette reading</th>
<th>Vol.of Thio (ml)</th>
<th>Concordant value (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0</td>
<td></td>
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<td></td>
<td>0</td>
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</tbody>
</table>

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Similarly, Quantity of oxygen in incubated sample

\[ \text{Quantity of oxygen} = \frac{X \times 0.025 \times 8 \times 1000}{200} \times \frac{x}{10} \]

DO = \text{_________ g/lt.}

BOD = \text{DO before inc.} - \text{DO after inc.}

= \text{_________ - _________ mg/l.}

(Significance of 0.025 N thio = 1ml of 0.025 N thio = 1 mg/l of DO)

---

**ESTIMATION OF COD**

Principle: COD is the measure of oxygen consumed during the oxidation of oxidisable organic matter by a strong oxidising agent in the presence of \( \text{H}_2\text{SO}_4 \).

The sample is refluxed with \( \text{K}_2\text{Cr}_2\text{O}_7 \) and \( \text{H}_2\text{SO}_4 \) in the presence of mercuric sulphate to neutralise the effects of chlorides and silver sulphate as catalyst. The organic matter gets oxidised completely by \( \text{K}_2\text{Cr}_2\text{O}_7 \) in the presence of silver sulphate to produce \( \text{CO}_2 \) and water. The excess dichromate after the reaction is titrated against ferrous ammonium sulphate. The dichromate consumed gives the oxygen required for the oxidation of organic matter.

**Reagents**

i) Sulphuric acid - silver sulphate solution

Dissolve 22g silver sulphate in 4.1 kg bottle of Conc. \( \text{H}_2\text{SO}_4 \). It will take 1 or 2 days for the silver sulphate to dissolve.
ii) Potassium dichromate solution (0.25 N)

Dissolve 12.25 g of K₂Cr₂O₇, previously dried at 103°C for 2 hours in distilled water and make upto 1 litre.

iii) Ferroin indicator

iv) Ferrous ammonium sulphate solution (0.025N)

Dissolve 98g of ferrous ammonium sulphate in distilled water. Add 20ml of Conc. H₂SO₄, cool and make upto 1 litre. The solution must be standardised against K₂Cr₂O₇ daily.

v) Mercuric sulphate solution

0.4g of Hg₂SO₄ is added to 30ml of Conc. H₂SO₄ and mix well.

Procedure

i) Standardisation of FAS

Pipette 10ml of 0.25N K₂Cr₂O₇ into a conical flask and dilute with distilled water to about 100ml. Add 30ml conc. H₂SO₄ and allow to cool. Titrate against ferrous ammonium sulphate using two or three drops of ferroin indicator. Take as the endpoint of the titration the first sharp colour change from blue green to reddish brown. Record the volume of FAS used in titration.

Estimation of COD

a) Add a few clean glass beads to dry round bottom flask. Pipette a 10ml of sample in the flask, add 0.4g mercuric sulphate and add 10ml of
0.25N $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Carefully add 30ml of Conc. $\text{H}_2\text{SO}_4$ silver sulphate reagent and mix. Attach the flask to the condenser and reflux the mixture for 2 hours. Cool and then wash down the condenser with about 25ml of distilled water.

b) Dilute the mixture to about 140ml, cool to room temperature and titrate the excess dichromate with ferrous ammonium sulphate solution using the ferroin indicator. Take as the endpoint of the titration, the sharp colour change from blue green to reddish brown, even though the blue-green may reappear within minutes. Record the volume of FAS solution used for the sample.

c) A blank consisting of 10ml of distilled water instead of the sample, together with the reagents, is refluxed in the same manner. Record the volume of FAS solution used for the blank.

**Calculation**

<table>
<thead>
<tr>
<th>Vol of Sample (ml)</th>
<th>Burette reading</th>
<th>Vol.of FAS (ml)</th>
<th>Concordant value (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Blank (10ml)</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>

Difference in volume of FAS required in the blank and sample

= \( V_{\text{blank}} - V_{\text{sample}} \)

= \( X \) ml

1000 ml of 1N FAS

= \( 8 \) g of oxygen
.

\[
\text{10 ml sample contains } = \frac{X \times 0.1 \times 8}{1000} \text{ g of oxygen}
\]

\[
\therefore \text{1000 ml sample contains } = \frac{X \times 0.1 \times 8}{1000} \times 1000 \text{ g of oxygen}
\]

COD = \underline{\text{\(\frac{}{}\)}} \text{ g of oxygen}

COD = \underline{\text{\(\frac{}{}\)}} \times 1000 \text{ mg/l of oxygen}

\section*{ESTIMATION OF CHLORIDE}

Principle: In a neutral or slightly alkaline solution, potassium dichromate can indicate the endpoint of AgNO\textsubscript{3} titration of chloride. AgCl is precipitated quantitatively before red silver chromate is formed.

\textbf{Reagents}

i) \(\text{K}_2\text{CrO}_4\) indicator solution

Dissolve 5g of \(\text{K}_2\text{CrO}_4\) in little distilled water. Add AgNO\textsubscript{3} soln. until a definite red ppt is formed. Let the sample be filtered and diluted to 100ml with distilled water.

ii) Standard AgNO\textsubscript{3} solution (0.1N)

Dissolve 1.69 g in 100 ml of distilled water.
Procedure

20ml of the given sample is pipetted out into a clean conical flask. Few drops of K$_2$CrO$_4$ indicator is added and the solution is titrated against silver nitrate. The end point is the colour change from yellow to brick red.

Calculation

<table>
<thead>
<tr>
<th>Vol of Sample (ml)</th>
<th>Burette reading</th>
<th>Vol of AgNO$_3$ (ml)</th>
<th>Concordant value (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
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<tr>
<td>20</td>
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<td>20</td>
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</table>

Amount of Chloride = \( \frac{\text{Vol}_{\text{AgNO}_3} \times N_{\text{AgNO}_3} \times \text{Eq.Wt. Cl} \times 1000}{\text{vol of sample}} \)

ESTIMATION OF SULPHATE

Principle: Sulphate ion is precipitated in the form of barium sulphate crystals of uniform size in acid medium when glycerol-ethanol solution is added as a stabilizer. The concentration of the absorbance of light by barium sulphate is found out by using spectronic 20 at 420 nm.

Reagents

i) Standard Na$_2$SO$_4$ solution
Dissolve 1.42 g of Na$_2$SO$_4$ in 100ml
ii) NaCl - HCl solution

60g of NaCl is dissolved in 100ml of distilled water. To this add 5ml of Conc. HCl and final volume is made upto 200ml.

iii) Glycerol - ethanol solution

50ml of glycerol is added to 100ml of ethanol.

Procedure: 2g of barium chloride is added to 100ml of the sample. To this, 5ml of NaCl-HCl solution and 5ml of ethanol - glycerol solution are added and immediately kept in the magnetic stirrer for 1 minute. Read the absorbance at 420nm in a spectronic 20 using a suitable blank.

Simultaneously the OD of the standard is also determined.

**Calculation**

\[
\text{Sulphate (mg/l)} = \frac{\text{OD of Sample}}{\text{Standard OD}} \times 0.02 \times 1000
\]

\[
= \underline{\text{__________mg/l}}
\]

**TOTAL PHOSPHORUS**

**Reagents**

1. Con. HNO\textsubscript{3}
2. HClO\textsubscript{4}
3. Dil H\textsubscript{2}SO\textsubscript{4}
4. Ammonium Molybdate solution
Part A : 25g ammonium molybdate in 175ml of distilled water.

Part B : Add 250ml of Conc. $\text{H}_2\text{SO}_4$ to 400ml of distilled water and cool.

Mix the solution A and B, dilute it to 1 litre.

5. Stannous chloride : 2.5g of stannous chloride is dissolved in 100ml of glycerol. Heat on a water bath for rapid dissolution.

Procedure

Take 25ml of the sample and digest with 5ml of Conc. $\text{HNO}_3$ and 5ml of perchloric acid, heat on a hot plate until nearly dry. Now cool the china dish and add 5ml of dil. $\text{H}_2\text{SO}_4$, boil for 10 minutes and cool. Then filter the contents through whatmann filter paper in a 250 ml standard flask and make it upto the mark with distilled water.

Take 50ml of the made up solution and add 2ml of ammonium molybdate solution followed by the addition of 5 drops of stannous chloride solution. Swirl the flask and leave it for 10 minutes. Take the optical density at 690 nm.

TOTAL NITROGEN

Reagents

1. Conc. Sulphuric acid
2. $\text{HCl}$ (0.1N)
3. Digestion catalyst: Grind together 20g CuSO$_4$, 3g mercuric oxide and 1g gel powder, mix thoroughly one part of this mixture with 20 parts of sodium sulphate or potassium sulphate.

4. Boric acid and mixed indicator.

Prepare 4% solution of boric acid by dissolving 4g of boric acid in 100ml distilled water.

Mix alcoholic solution of bromocresol green (0.5%) and methyl red (0.1%) in 2:1 ratio. Add 5ml of mixed indicator in a 100ml boric acid only when the colour becomes blue, adjust the pH with 0.01N HCl until the colour just turns faint pink to brown.

**Procedure**

I. **Digestion**

25ml of sample is taken a kjeldahl flask. This was added with 10ml of catalyst and 5ml of conc. H$_2$SO$_4$ and mixed by gentle swirling. Initially this is heated at low temperature for 10-30 minutes, until the frothing stops. The temperature is raised and the digestion is continued to release all the residual nitrogen. The flask is cooled and the volume is made upto 100ml.

II. **Distillation**

Steam distillation is done in the parnes wegener distillation unit. This unit consists of round bottom flask which is connected to a distillation flask, with two valves. It is inturn connected to a distillation condenser. There are outlets for steam when unused and an opening for introducing the digested sample.
25ml of the digested sample is introduced through a funnel and 10ml of 40% NaOH is added. The beaker containing boric acid and mixed indicator is placed below the condenser and seen that the tip of the condenser is dipped well in the solution. When the distillation is over, 25ml of the condensate is collected and the beaker is removed before stopping the steam generation to prevent back sucking.

III. Estimation by Titration

The boric acid with dissolved ammonia is titrated against 0.1N HCl. The endpoint is the colour change to light brown of reddish pink. A blank titration is done with distilled water.

Calculation

<table>
<thead>
<tr>
<th>Vol of Sample (ml)</th>
<th>Burette reading</th>
<th>Vol of HCl (ml)</th>
<th>Concordant value (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td></td>
</tr>
</tbody>
</table>

\[
N = \frac{V_{(Sample - blank)} \times N_{HCl} \times 1.4 \times 1000}{\text{vol. of sample taken}}
\]

= ___________ mg/l