الشركة القابضة
لمياه الشرب والصرف الصحي

برنامج المسار الوظيفي
للعاملين بقطاع مياه الشرب والصرف الصحي

دليل المتدرب

التحاليل الفيزيائية والكيميائية

كيمائي صرف-درجة ثالثة

حقوق الطبع محفوظة
الشركة القابضة لمياه الشرب والصرف الصحي
الإدارة العامة للمسار الوظيفي - إدارة الصناع

تم إعداد المادة بواسطة الشركة القابضة لمياه الشرب والصرف الصحي
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Contents

Physical analysis:

1- Alkalinity

Introduction

This method is taken from the Standard Methods for the examination of water and wastewater edition 20, 2320 B."Titration method".

Alkalinity of water is its acid-neutralizing capacity, and is a measure of the sum of all titratable bases. Hydroxide, carbonate, bicarbonate, borate, Phosphate, silicate and other bases may contribute to the measured alkalinity.

Alkalinity is useful in determining the tendency of water to dissolve or precipitate scale and monitoring anaerobic digestion processes. Properly operating anaerobic digesters typically have supernatant alkalinities in the range 2000 to 4000 mg $CaCO_3$

Principle

Total alkalinity determined by titration. For sewage the sample is diluted and titrated directly. Although the total alkalinity is usually expressed empirically as calcium carbonate, it consists largely of ammonium bicarbonate alkalinity but also includes other carbonates and bicarbonates, salts of volatile acids and ions such as phosphates.

Interference

Substances usually present at their normal concentration in these types of samples do not cause interference with the total alkalinity determination.

Scope

This procedure describes how to measure Total Alkalinity especially in anaerobic conditions in basic tanks.

Personal Responsible

Title	Chemist
Responsibilities	Responsible to measure Total Alkalinity in wastewater samples.

Hazards

- Laboratory coats must be worn at all times.
- This method involves handling of strong acids. Gloves and protective clothing must be worn.
- Many harmful micro-organisms can be found in sludge, care and cleanliness therefore are essential.

Reagent and Chemicals :

Water: Laboratory distilled water.

Approximately 0.05 N sodium carbonate standard solutions:

1. Weigh 2.5 g ± 0.20 of sodium carbonate (anhydrous) which has been previously dried in oven at 105 ± 5 ºC for four hours, and cooled in a desiccator.
2. Transfer to a 1L volumetric flask, through a glass funnel, with a stream of distilled water. Make up to the mark with distilled water, mix and dissolve.
3. This solution is stable for 1 week. Mark with the expiry date.

Standard sulfuric acid, 0.1 N

1. Transfer by measuring flask about 700 ml of distilled water to a 1L beaker. Then pipette to the beaker. Then pipette with stirring 2.8 ml of concentrated sulfuric acid to the beaker.
2. Allow the sulfuric acid solution to cool, then transfer to a 1L volumetric flask and make up to the mark with distilled water.
3. This solution is stable for one week, mark with the expiry date.

Quality Control Standard- Stock Alkalinity QC (equivalent to 1000 mg/l $CaCO_3$)

1. Weight out 1.059 ± 0.001 g of sodium carbonate (anhydrous) previously dried at 105 ± 5 ºC for 1-2 hours.
2. Cooled in desiccators.
3. Transfer to a 1 liter volumetric flask, dissolve in water, then make up to the mark with water and mix well.
4. Store in a stopper glass bottle at 4 ºC.
5. This solution is stable for 3 months. Mark with the expiry date.

Alkalinity QC solutions (150 mg/l $CaCO_3$)

1. Transfer 15.0 ± 0.1 ml solution 2.2 to a 100 ml volumetric flask and make up to the mark with distilled water.
2. Store at 4 ºC. This solution is stable for 1 month. Mark with the expiry date.

Note:

The quality control standard must not be prepared by the same person who is carrying out the analysis.

Equipment and supplies:

1. Drying oven
2. Analytical balance
3. Desiccators
4. Magnetic stirrer / hot plate
5. pH meter

6. Burette, 50 ml
7. 1000 ml volumetric flasks
8. Pipettes of various sizes
9. Measuring cylinders
10. Glass funnels

Procedures

Quality Control Checks for Alkalinity

- One quality control check is to be run with every batch of samples; this is the Quality Control standard and control chart.
- Quality control checks for the PH meter must be run according to the PH procedure SP_L_02.
- A blank determination must also be run with every batch of samples.

Alkalinity Quality Control Chart

- A quality control standard (QC) must be run with each batch of samples.
- The target concentration used is 150 mg/l Ca CO_3.
- The QC must be prepared with reagents independent of the reagents used for calibration.
- An analyst, independent of the analyst who prepared the standards for calibration must prepare the QC standard solution.

Preparation of the Quality Control Standard.

- Use of control chart
- A "Shewert" Control chart has been set up using the standard solution at 150 mg/l $CaCO_3$ as the target concentration.
- For a more detailed explanation of quality control charts and how they should be used refer to document SP_L_02 "Quality Control Charts".
- Plot the result from the Quality Control Standard onto the control chart as soon as the result is available.

Note:

Quality Control Checks are not currently run for sewage sludge Alkalinity.

Standardization of standard 0.02 N sulfuric acid Solution:

1. Calibrate the pH meter using the pH meter procedure LP/06

2. Take, by volumetric pipette, 40 ml of 0.05 N Na_2CO_3 solution and transfer to a 250 ml beaker.
3. Add, by measuring cylinder, approximately 60 ml of distilled water to the beaker.
4. Start stirring, then place the pH combined electrode in the beaker.
5. Fill the burette with 0.02 N standard sulfuric acid solution and titrate against the 0.05 Na_2CO_3 solution to pH of about 5.
6. Lift the pH electrode, rinse into the same breaker and boil gently for 3 to 5 min.
7. Cool to room temperature, and then replace the pH electrode in the beaker with stirring.
8. Continue titration with 0.02 N sulfuric acid solution to pH in the range 4.3 to 4.7 and record the volume.

$$\text{Normality (N)} = \frac{\text{A} \times \text{B}}{53.0 \times \text{C}}$$

Where:

A = g Na_2CO_3 weighed into 1L flask

B = ml Na_2CO_3 solution taken for titration

C = ml acid used.

1 ml 0.02 N standard sulfuric acid ≡ 1.00 mg $CaCO_3$

Sample measurement water sample

1. A blank distilled water sample must be analyzed with each batch of sample.
2. A quality control standard must be analyzed with each batch sampler.
3. Transfer an appropriate volume of sample to a 250 ml beaker by measuring cylinder.
4. Start stirring and place the combined electrode in the beaker.
5. Fill the burette with 0.02 N standard sulfuric acid solution and titrate against the sample unit the pH reading is 4.5.
6. Carry out a blank determination using distilled water in place of the sample.
7. Calculation of Alkalinity for Sewage

$$\text{Alkalinity as mg } CaCO_3 = \frac{\text{A} \times \text{N} \times 50000}{\text{ml of sample}}$$

Where:

A = ml of standard sulfuric acid used.

N = normality of the standard acid.

Quality control standard

Transfer an appropriate volume of QC standard to a 250 ml beaker by measuring cylinder and titrate it.

Quality Control Checks - Sewage Samples

Plot the quality control standard result on the quality control chart and check that the standard meets the quality requirements (detailed in SP_L_02 quality control charts Laboratory procedures), if the quality requirements are not met then report the failure to the Senior Scientist and Laboratory Manager. You must not report the results.

Standardization of standard 0.1 N sulfuric acid solution

1. Take, by volumetric pipette, 40 ml of 0.05 N Na_2CO_3 solution and transfer to a 250 ml beaker.
2. Add by measuring cylinder approximately 60 ml of distilled water to the beaker.
3. Start stirring and place the pH-combined electrode in the beaker.
4. Fill the burette with 0.1 N standard sulfuric acid solution and titrate against the 0.05 N Na_2CO_3 solution to about pH 5.
5. Lift the pH electrode, rinse into the same beaker and boil gently for 3 to 5 min.
6. Cool to room temperature, then replace the pH electrode in the beaker with stirring.
7. Continue titration with 0.1 N standard sulfuric acid solution to pH in the range 4.3 to 4.7 and record the volume.

$$\text{Normality (N)} = \frac{A \times B}{53 \times C}$$

Where:

A = g Na_2CO_3 weighed into 1L flask

B = ml Na_2CO_3 solution taken for titration

C = ml acid used

1 ml 0.1 N standard sulfuric acid ≡ 5 mg $CaCO_3$

Analysis of sewage samples

1. Use a pipette or graduated cylinder to place 50 ml of sample in 100 ml beaker.
2. Fill burette with 0.1 or 0.02 N sulfuric acid.
3. Take a properly calibrated pH meter and with constant mixing of beaker contents, titrate to pH 4.5 with the sulfuric acid from the burette.
4. Record on the Alkalinity work sheet, the volume of titrant added to the end-point.
5. Carry out a blank determination in place of the sample.
6. Calculation of Alkalinity for Sewage Sludge.

$$\text{Alkalinity(as } CaCO_3) = \frac{A \times N \times 50}{\text{ml of sample}}$$

Where:

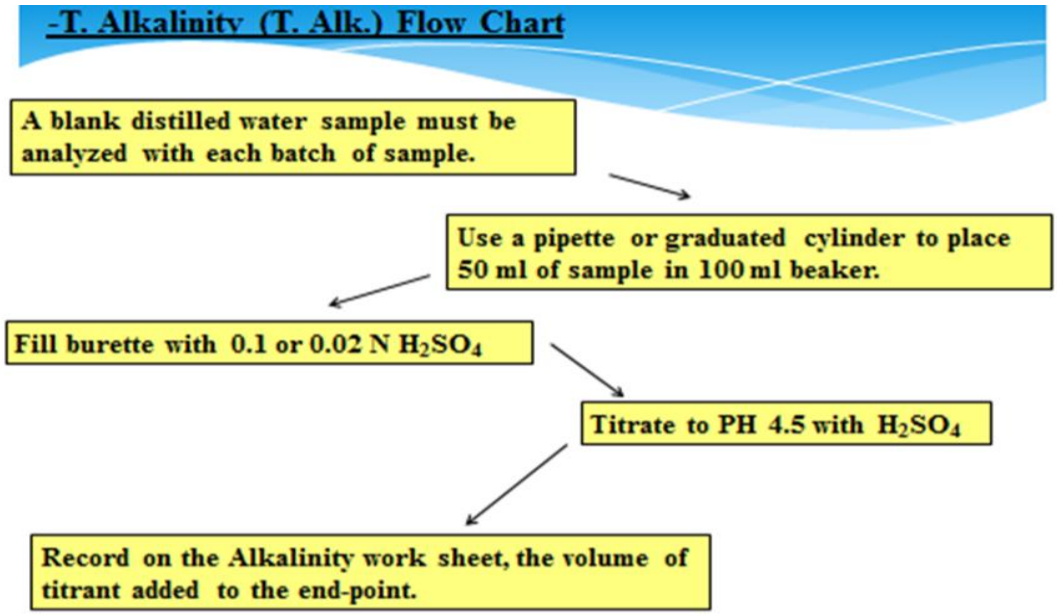
A= ml of standard sulfuric acid

N= Normality of standard acid.

Reporting Results

1. If all the quality checks meet the requirements then report the results.
2. All results must be reported to 1 decimal place.
3. If any Alkalinity results are less than 20 mg/L report the result as "less than 20 mg/l or < 20 mg/L".
4. Enter all data from the Alkalinity work sheet into the Alkalinity spread sheet on the computer.
5. Save the spread sheet and print out the Alkalinity report sheet. Pass to the Senior Scientist or Laboratory Manager to sign off.
6. When the Alkalinity report sheet has been signed off the daily report sheet can be prepared

Flow chart:



2- Conductivity

Principal

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, on their total concentration, Conductance (the reciprocal of resistance) of solution is measured between two fixed and chemically inert electrode the conductance of absolution, Gist directly proportional to the electrode surface area and inversely proportional to the distance between the electrodes L, cm.

The constant of proportionality, K

$$G=K\ (A/L)$$

- To compare conductivities, value of K is reported relative to electrode with $A=1cm^2$ and L=1cm.
- Cells of different physical configuration are characterized by their cell constant, with cell constant of k =1.0.
- The actual k of a specific cell is determined by a comparison measurement of standard solution of known of conductivity (e.g., 0.01 M KCl).
- The cell constant k must be multiplied by the observed conductance to obtain the actual conductivity reading.
- The conductivity of a solution will change with a change in temperature.
- The temperature is chosen as a reference to be either 25°C or 20°C
- As soon as the samples are delivered to the laboratory start the analysis immediately,

Scope

Water and wastewater inlet and outlet samples.

Reagents and Chemicals :

- Standard potassium chloride solution, KCl, 0.01 M:

Weigh accurately 745.6 mg anhydrous potassium chloride solutions, KCl (dried before at 105 °C for an hour) and dissolve in distilled water. Transfer into volumetric flask and complete to the mark with distilled water. This standard has conductivity of 1412 µ mhos/cm.

Equipment and supplies:

- Conductivity meter (the conductivity cell has a platinum –electrodes)
- Volumetric flasks.
- Beakers
- Magnetic stirrers
- Stirrer bars
- Platonizing unit kit

Procedures

1. Calibration:

- Follow the instruction manual of Apparatus Company.

2. Conductivity measurements:

- Press the MODE to place the meter in conductivity mode (check the temperature is compensated by the temperature compensated cell).
- Rinse the probe with distilled water insert into the sample solution. Make sure air bubbles are not entrapped near the probe with stirring.
- Record the reading when it stabilizes

3- Cleaning the probe

- If the sample contains oils, grease, or fats, the probe is cleaned with dipping in 1:1 hydrochloric acid solution and rinse with dematerialized water

Reporting Results:

- Record the electric conductivity value as soon as meter stabilizes

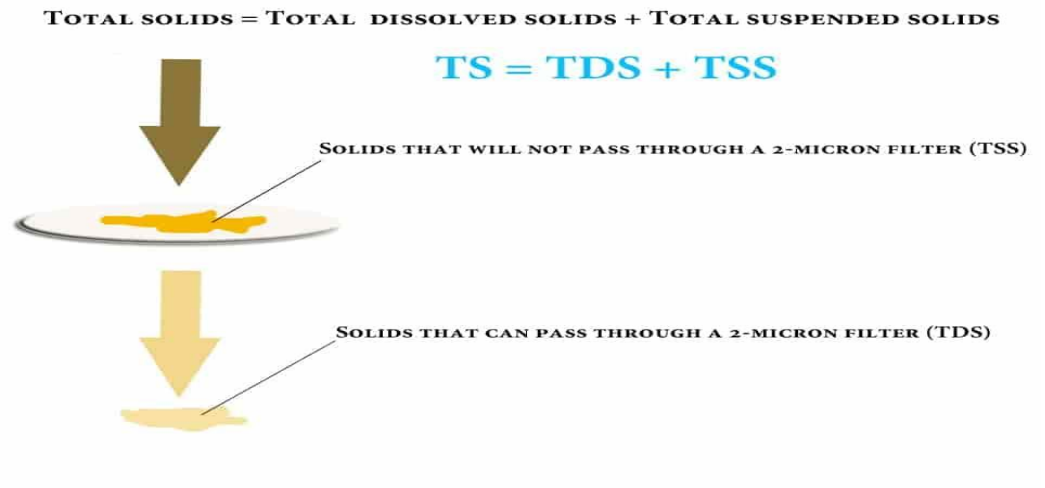
3- Solids Determination:

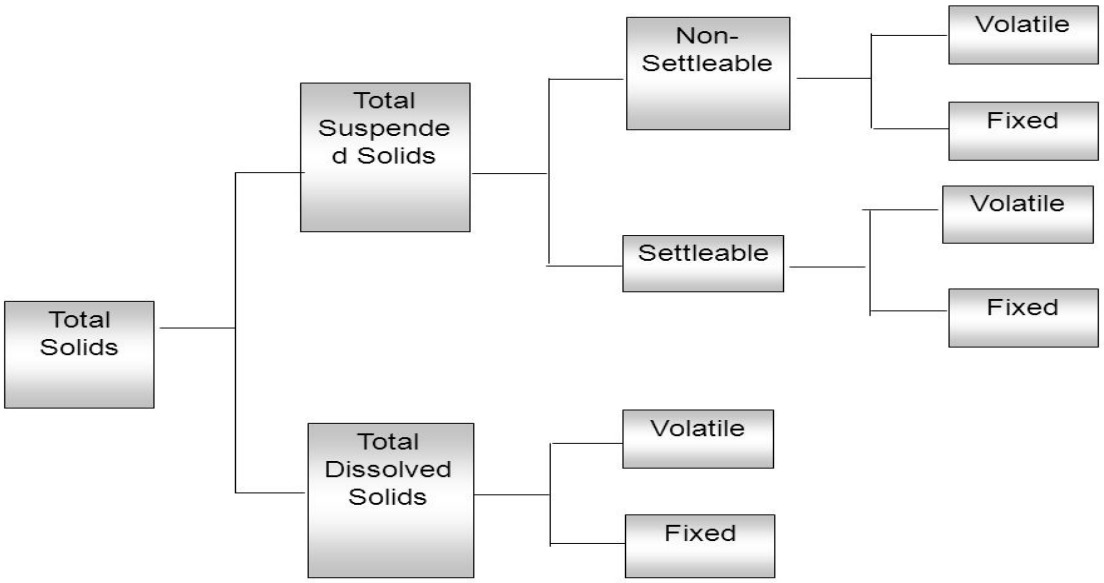
- Discharges of wastewater into the environment are monitored for solids content because of their impact on aquatic life and usefulness of the water being affected.
- Solids are also monitored at various locations in wastewater treatment plants so that process control may be optimized and efficiency determined.
- The material left in a sample vessel after evaporation and subsequent oven drying at a defined temperature is total solids.

Total solids include:

- Total suspended solids (TSS)—the portion of total solids in an aqueous sample retained on the filter. NOTE: Some clays and colloids will pass through a 2 µm filter.
- Total dissolved solids (TDS)—the portion of total solids in a water sample that passes through a filter with a nominal pore size of 2 µm filter.

- Whether a solids particle is filtered into the "suspended" or "dissolved" portion principally depends on a filter's thickness, area, pore size, porosity, and type of holder, as well as the physical nature, particle size, and amount of solids being filtered





- Volatile solids—the total, suspended, or dissolved solids lost from a sample after ignition for a specified time at a specified temperature.
- Fixed solids—the total, suspended, or dissolved solids remaining in a sample after ignition for a specified time at a specified temperature.
- Settle able solids—the material in a sample that settles out of suspension within a defined period.

3-1 Total Solids (Dried at 103–105°C)

Principle:

- A well-mixed sample is evaporated in a weighed dish and dried to constant weight in an oven at 103 to 105°C.
- The increase in weight over that of the empty dish represents the total solids.
- The results may not represent the weight of actual dissolved and suspended solids in wastewater samples.

Interferences:

- Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.
- Exclude large, floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result.

- Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis.

Equipment and supplies:

- Evaporating dishes: Dishes of 100-ml capacity made of one of the following materials:
- Porcelain, 90-mm diam.
- Platinum—Generally satisfactory for all purposes.
- High-silica glass
- Muffle furnace for operation at 550°C.
- Steam bath.
- Desiccator
- Drying oven, for operation at 103 to 105°C.
- Analytical balance, capable of weighing to 0.1 mg.
- Magnetic stirrer with TFE stirring bar.
- Wide-bore pipets
- Graduated cylinder.
- Low-form beaker

Procedure:

1- Preparation dishes:

- If volatile solids are to be measured ignite clean evaporating dish at 550°C for 1h in a muffle furnace.
- If only total solids are to be measured, heat clean dish to 103 to 105°C for 1h.
- Store and cool dish in desiccator until needed. Weigh immediately before use.

2- Sample analysis:

- For homogeneous samples, pipet from the approximate midpoint of the container but not in the vortex.
- Choose a point both mid depth and midway between wall and vortex.
- Evaporate to dryness on a steam bath or in a drying oven.
- When evaporating in a drying oven, lower temperature to approximately 2°C below boiling to prevent splattering.
- Dry evaporated sample for at least 1h in an oven at 103 to 105°C, cool dish in desiccator to balance temperature, and weigh.

- Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained, or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less.
- Analyze at least 10% of all samples in duplicate.
- Duplicate determinations should agree within 5% of their average weight.

Calculation:

$$\text{mg total solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

Where:

- A = weight of dried residue + dish, mg.
- B = weight of dish, mg.

References:

- Ref: Standard Methods 23rd Edition,2017. 2540-B SOLIDS.

3-2 Total Suspended Solids Dried at 103–105°C

Introduction and definition:

- **Total suspended solids (TSS):** The portion of total solids in an aqueous sample retained on the filter. NOTE: Some clays and colloids will pass through a 2 µm filter.
- **Method Blank (MB):** a sample of laboratory pure water containing no target analyte that is taken through the entire sampling and analytical procedure. In this case, dilution water is used as the blank. The analysis of a method blank helps identifies any contamination introduced in the analysis process.
- **Duplicate sample:** select routine samples to be analyzed twice. Independently prepare and analyze duplicate samples. Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples. Calculate control limits for duplicates when methods specific limits are not provided.
- **Laboratory fortified blank (LFB)**
- Sample with known concentration of analyte that is used to asses the performance of total analytic system

Principle

- This method is taken from The Standard Methods for the Examination of Water and Wastewater AWWA 23TH edition (2540 D. Total Suspended Solids Dried at 103–105°C).
- A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, it may be necessary to increase the diameter of the filter or decrease the sample volume. To obtain an estimate of total suspended solids, calculate the difference between total dissolved solids and total solids.
- This procedure is suitable for the analysis of sewage, industrial effluent and river water samples.
- This method is suitable for the determination of solids in potable and surface waters and wastewaters with total suspended solids (TSS) of 20 to 20,000 mg/L.

Interferences

- Highly mineralized water:
  - with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.
- Exclude large, floating particles or submerged agglomerates:

- of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result.

- Floating oil and grease:
  - Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

- Two-phase or three-phase samples:

- Make and keep such samples homogeneous during transfer. Use special handling to ensure sample integrity when subsampling. Mix small samples with a magnetic stirrer.

- If suspended solids are present, pipet with wide-bore pipets If part of a sample adheres to the sample container, consider this in evaluating and reporting results.

Some samples dry with the formation of a crust that prevents water evaporation; special handling is required to deal with this.

- The temperature

- Because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating.

- Desiccation

- Some samples may be stronger desiccants than those used in the desiccator and may take on water.

Residues dried at 103 to 105°C may retain not only water of crystallization but also some mechanically occluded water. Loss of CO2 will result in conversion of bicarbonate to carbonate. Loss of organic matter by volatilization usually will be very slight. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

Residues dried at 180 _+- 2°C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of CO2 results from conversion of bicarbonates to carbonates and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost. In general, evaporating and drying water samples at 180°C yields value for dissolved solids closer to those obtained through summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.

- To rinse filters and filtered solids and to clean lab ware use Type III water. Special samples may require a higher quality water.
- Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.

Hazard and Precaution
NA

Reagents and Chemicals:

Laboratory fortified blank: (200 mg/l QC Suspended Solids Stock)

- Weigh out 0.2000 ± 0.001g of GFC grade filter paper, which has been previously dried in an oven at 105 ± 5°C for a minimum of one hour, and then allowed to cool in a desiccator for a minimum of 10 minutes.
- Weighing out the exact amount of filter paper is achieved by placing two 4.7 cm GFC filter papers on the analytical balance and then either tearing small amounts of the paper off, or adding small pieces of another filter paper until the required weight is achieved.
- Transfer the required weight of filter paper to a liquidizer and add approximately 200ml of deionized water.
- Liquidize for one minute ± 15 seconds until a fine homogenous suspension is produced.
- Quantitatively transfer the suspension to a one litre volumetric flask and make up to the mark.
- This suspension must be vigorously shaken immediately before use.
- This suspension is stable for 7 days. Mark with the expiry date.
- If a liquidizer is not available then the filter paper can be ground using a pestle and mortar with a small volume of water

20 mg/l QC Suspended Solids Suspension:

- Using a suitable measuring cylinder transfer 50 ± 5ml of well shaken 200 mg/l Suspended Solids Stock into a 500 ml volumetric flask.
- Make up to the mark with pure water.
- This suspension must be well shaken before use, and is stable for 2 days.
- Mark with the expiry date.

Equipment and supplies:
apparatus:

a. Filtration apparatus:

- One of the following, suitable for the filter disk selected:

- Membrane filter funnel.
- Gooch crucible, 25-mL to 40-mL capacity, with Gooch crucible adapter.
- Filtration apparatus with reservoir and coarse (40- to 60-m) fritted disk as filter support.
- Suction flask, of sufficient capacity for sample size selected

b. Drying oven controlled at 103 to 105°C

c. Analytical balance capable of weighing to 0.1mg.

d. Thermometer

e. Magnetic stirrer with TFE stirring bar.

Glassware:

a. Wash bottle for distilled water

b. Desiccator, provided with a desiccant containing a color indicator of moisture concentration or an instrumental indicator.

c. Graduated cylinder, 25, 50,100, 250, 500 and 1,000ml.

d. Volumetric flasks 1000ml and 2000ml.

e. Low-form beaker (Class B or better)

f. Pestle and Mortar

g. Aluminum weighing dishes

h. Watch Glass

i. Forceps

j. Glass-fiber filter disks without organic binder.

Safety

- **Safety tools**

Due to various hazards in the laboratory, safety glasses must be worn at all times. Be careful when using the oven at elevated temperatures to avoid burns. Use the tongs to remove the evaporating dish/crucible from the oven

- **Waste Disposal**

Dispose of sample waste down the drain with copious amounts of water

Sampling:

- **Sample Storage**

Measurement	Minimum Sample Size mL	Container	Sample Type	Preservation	Maximum Storage Recommended
Solid	200	P, G	c	Cool<=6°C	7 d

- **Sample handling**

The samples obtained from the sampling coordinator and after check by the lab staff

Procedure:

- **Preparation of evaporating dish:**

- If volatile solids are to be measured ignite clean evaporating dish at 550°C for 1 h in a muffle furnace. If only total solids are to be measured, heat clean dish to 103 to 105°C for 1 h.
- Store and cool dish in desiccator until needed. Weigh immediately before use.

- **Preparation of glass-fiber filter disk:**

- If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up in filtration apparatus.
- Apply vacuum and wash disk with three successive 20-mL portions of reagent-grade water. Continue suction to remove all traces of water, turn vacuum off, and discard washings.
- Remove filter from filtration apparatus and transfer to an inert aluminum weighing dish.
- If a Gooch crucible is used, remove crucible and filter combination.
- Dry in an oven at 103 to 105°C for 1 h..
- Cool in desiccator to balance temperature and weigh.
- Repeat cycle of drying or igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less.
- Store in desiccator until needed.

- **Sample analysis:**

- Choose sample volume to yield between 2.5 and 200 mg dried residue. If volume filtered fails to meet minimum yield, increase sample volume up to 1 L.
- For method blank determination: use 1 liter of PURE water
- For determination: use 100 ml of 20 mg/l QC Suspended Solids Suspension

- If complete filtration takes more than 10 min, increase filter diameter or decrease sample volume.
- Sample analysis: Assemble filtering apparatus and filter and begin suction.
- Wet filter with a small volume of reagent-grade water to seat it.
- Stir sample with a magnetic stirrer at a speed to shear larger particles, if practical, to obtain a more uniform (preferably homogeneous) particle size.
- Centrifugal force may separate particles by size and density, resulting in poor precision when point of
- sample withdrawal is varied.
- While stirring, pipet a measured volume onto the seated glass-fiber filter. For homogeneous samples,
- pipet from the approximate midpoint of container but not in vortex.
- Choose a point both mid depth and midway between wall and vortex.
- Wash filter with three successive 10-mL volumes of reagent- grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete.
- Samples with high dissolved solids may require additional washings.
- Carefully remove filter from filtration apparatus and transfer to an aluminum weighing dish as a support.
- Alternatively, remove the crucible and filter combination from the crucible adapter if a Gooch crucible is used.
- Dry for at least 1 h at 103 to 105°C in an oven, cool in a desiccator to balance temperature, and weigh.
- Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until the weight change is less than 4% of the previous weight or 0.5 mg, whichever is less. One sample must be run as duplicate

- **Calculations**

mg total solids/L = (A -B) -1000)/ sample volume, mL

Where:

A= weight of filter + dried residue, mg

B = weight of filter, mg.

- **LFB recovery:**

(Cb/ I) * 100 =Recovery LFB

Where:

Cb = LFB concentration determined experimentally

I = initial concentration from analytes added to LFB.

- **Relative percent difference:**

$((D1 \_ D2)/((D1 + D2)/ 2))*100 = \%RPD$

where:

D1 = concentration determined for first duplicate, and

D2 = concentration determined for second duplicate

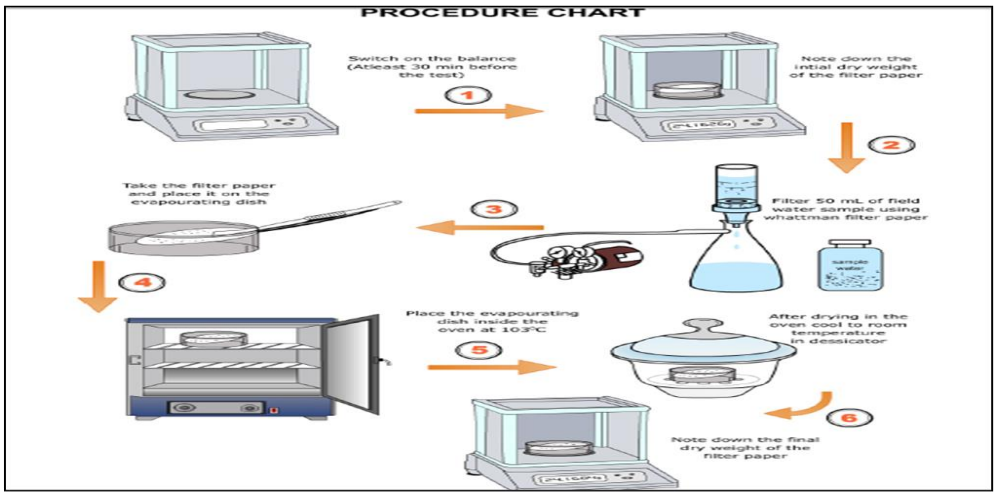
- **Quality Control**

QC for method	frequency	Acceptance Criteria	Corrective Action:
Method Blank	once per analysis batch	If method blank is <1/2 RL	Re analyze alternative source of blank Check filter paper & filtration system Reanalyze all samples Check calculation. Report in bench sheet " these data are associated with a blank value that exceeds the detection limits
LFB		LFB recoveries: (according to the validation criteria)	All samples must be reanalyzed If There is not extra sample for reanalysis or holding time expired " the sample must be reported as No (result)"
Duplicates of the sample	at least 10% of all samples	%RPD within 5% of their average weight	

Reporting:

- TSS results <100 mg/l must be reported to 1 decimal place.
- TSS results >100 mg/l must be reported to the nearest whole number.
- The minimum reporting limit for suspended solids is 2 mg/l. Results below this must be reported as (<2.0 mg/l)

Flow chart:


PROCEDURE CHART
Switch on the balance (Atleast 30 min before the test)
1
Note down the intial dry weight of the filter paper
2
Filter 50 mL of field water sample using whattman filter paper
3
Take the filter paper and place it on the evapourating dish
4
Place the evapourating dish inside the oven at 103°C
5
After drying in the oven cool to room temperature in dessicator
6
Note down the final dry weight of the filter paper

3-3 Total Dissolved Solids in water samples

Introduction and definition:

- **Total Dissolved Solids (TDS):**Those solids capable of passing through a glass-fiber filter and dried to constant weight at 180^{o}C. Residue, filterable is an equivalent term
- **Method Blank :** A sample of laboratory pure water containing no target analyte that is taken through the entire sampling and analytical procedure. In this case, dilution water is used as the blank. The analysis of a method blank helps identifies any contamination introduced in the analysis process.
- **Duplicate sample :**Select routine samples to be analyzed twice. Independently prepare and analyze duplicate samples
- **Laboratory fortified blank (LFB) :**Sample with known concentration of analyte that is used to assess the performance of total analytic system

Principle

- This method is taken from The Standard Methods for the Examination of Water and Wastewater AWWA 23TH edition (2540 C). Total Dissolved Solids Dried at 180°C
- A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures. The results may not agree with the theoretical value for solids calculated from chemical analysis of sample.

Interferences

- Highly mineralized water

with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

- Exclude large, floating particles or submerged agglomerates

of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result.

- Floating oil and grease

Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

- Two-phase or three-phase samples

Make and keep such samples homogeneous during transfer. Use special handling to ensure sample integrity when subsampling. Mix small samples with a magnetic stirrer.

- If suspended solids are present, pipet with wide-bore pipets If part of a sample adheres to the sample container, consider this in evaluating and reporting results.
- Some samples dry with the formation of a crust that prevents water evaporation; special handling is required to deal with this.
- The temperature

because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating.

Desiccation.

Some samples may be stronger desiccants than those used in the desiccator and may take on water.

Residues dried at 103 to 105°C may retain not only water of crystallization but also some mechanically occluded water. Loss of CO2 will result in conversion of bicarbonate to carbonate. Loss of organic matter by volatilization usually will be very slight. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

Residues dried at 180 _+- 2°C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of CO2 results from conversion of bicarbonates to carbonates and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost. In general, evaporating and drying water samples at 180°C yields value for dissolved solids closer to those obtained through summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.

Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

Hazard and Precaution

NA

Chemical and Reagent:

- **Sodium chloride TDS Laboratory Control Sample, 165ppm (optional):**
- Dry sodium chloride in 105^0 C oven for 4 hrs.
- on watch glass Add *0.16485*g of NaCl to a 1L volumetric flask and dilute to the mark with laboratory pure water.

- Stir at least 30 minutes (until dissolved) and transfer the solution to a 1L bottle.
- Store under the TDS hood; the standard expires when empty

Equipment and Supplies

- **Equipment:**

  - Filtration apparatus: One of the following, suitable for the filter disk selected:
    - Membrane filter funnel.
    - Gooch crucible, 25-mL to 40-mL capacity, with Gooch crucible adapter.
    - Filtration apparatus with reservoir and coarse (40- to 60-m) fritted disk as filter support.
    - Suction flask, of sufficient capacity for sample size selected
    - Drying oven controlled at 103 to 105°C
    - Analytical balance capable of weighing to 0.1mg.
    - Thermometer
    - Magnetic stirrer with TFE stirring bar.

- **Glassware:**

  - Wash bottle for distilled water
  - Desiccator, provided with a desiccant containing a color indicator of moisture
  - concentration or an instrumental indicator.
  - Graduated cylinder, 25, 50,100, 250, 500 and 1,000ml.
  - Volumetric flasks 1000ml and 2000ml.
  - Low-form beaker (Class B or better.)
  - Pestle and Mortar
  - weighing dishes
  - Watch Glass
  - Forceps
  - Glass-fiber filter disks without organic binder

Safety

- **Safety tools**

  - Due to various hazards in the laboratory, safety glasses must be worn at all times. Be careful when using the oven at elevated temperatures to avoid burns. Use the tongs to remove the evaporating dish/crucible from the oven.

- **Waste Disposal**

  - Dispose of sample waste down the drain with copious amounts of water

Sampling:

- **Sample Storage**

Measurement	Minimum Sample Size mL	Container	Sample Type	Preservation	Maximum Storage Recommended
TDS	200	P, G	c	Cool<=6°C	7 d

- **Sample handling**

The samples obtained from the sampling coordinator and after check by the lab staf

Procedure:

- **Preparation of glass-fiber filter disk:**

- If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up into filtration apparatus.
- Apply vacuum and wash disk with three successive 20-mL volumes of reagent grade water.
- Continue suction to remove all traces of water. Discard washings.

- **Preparation of evaporating dish:**

- If volatile solids are to be measured, ignite cleaned evaporating dish at 550°C for 1 h in a muffle furnace.
- If only total dissolved solids are to be measured,
- Heat clean dish to 180 _+ 2°C for 1 h in an oven.
- Store in desiccator until needed. Weigh immediately before use.
- Selection of filter and sample sizes: Choose sample volume.
- To yield between 2.5 and 200 mg dried residue. If more than 10 min are required to complete filtration, increase filter size or decrease sample volume.

- **Sample analysis:**

- In method blank determination: use 1 liter of PURE water.
- In LFB determination: use 100 ml of 20 mg/l QC Suspended Solids Suspension
- Stir sample with a magnetic stirrer and pipet.

- Measured volume onto a glass-fiber filter with applied vacuum.
- Wash with three successive 10-mL volumes of reagent-grade water,
- Allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete.
- Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness on a steam bath or in a drying oven. If necessary,
- Add successive portions to the same dish after evaporation.
- Dry evaporated sample for at least 1 h in an oven at 180 _+ 2°C, cool in a desiccator to balance temperature, and weigh.
- Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less.
- One sample must be run as duplicate.
- Repeat all steps with LFB(twice)LFM

- **Calculations:**

mg total dissolved solids/L =((A - B)* 1000)/ sample volume, mL)

Where:

A = weight of dried residue +dish, mg.

B = weight of dish, mg.

LFB recovery:

(Cb/ I) * 100 =Recovery LFB

Where:

Cb = LFB concentration determined experimentally

I = initial concentration from analytes added to LFB.

Relative percent difference:

(D1 - D2/((D1 + D2)/ 2))*100 = %RPD

Where:

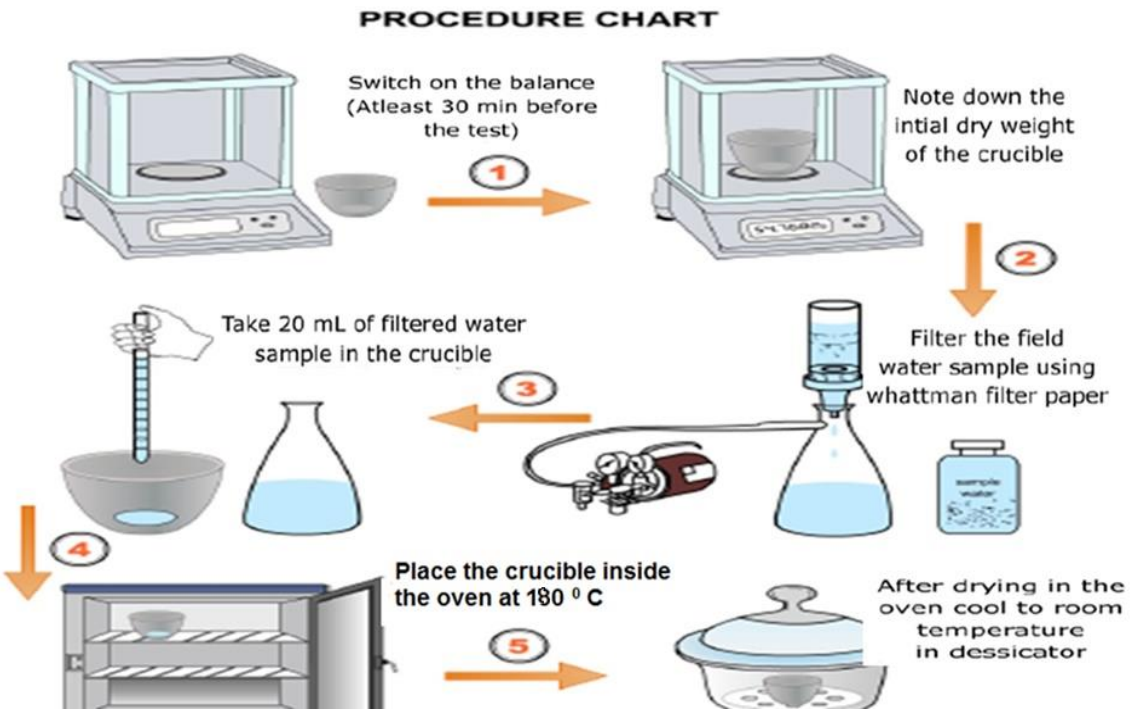
D1 = concentration determined for first duplicate, and

D2 = concentration determined for second duplicate

- **Quality Control**

QC for method	frequency	Acceptance Criteria	Corrective Action:
Method Blank	once per analysis batch	If method blank is <1/2 RL	Re analyze alternative source of blank Report in bench sheet " these data are associated with ablank value that exceeds the detection limits
LFB		LFB recoveries: (according to the validation criteria)	All samples must be reanalyzed If There is not extra sample for reanalysis or holding time expired " the sample must be reported as No result") Establish corrective actions)
Duplicates of the sample	at least 10% of all samples	%RPD within 5% of their average weight	

Flow chart:



3-4 Fixed and Volatile Solids Ignited at 550°C

Principle:

- This method is taken from The Standard Methods for the Examination of Water and Wastewater AWWA 23TH edition (2540 E. Fixed and Volatile Solids Ignited at 550°C)
- This procedure is suitable for the analysis of sewage, industrial effluent and river water samples.
- This procedure is applicable to VSS values between 20 and 2000 mg/L.
- The residue from Method (2540 B. Total Solids Dried at 103–105°C, 2540 C. Total Dissolved Solids Dried at 180°C, or 2540 D. Total Suspended Solids Dried at 103–105°C) is ignited to constant weight at 550°C. The remaining solids represent the fixed total, dissolved, or suspended solids while the weight lost on ignition is the volatile solids.
- The determination is useful in control of wastewater treatment plant operation because it offers a rough approximation of the amount of organic matter present in the solid fraction of wastewater, activated sludge, and industrial wastes**.**
- This method may be used to determine volatile suspended solids (VSS), total volatile solids (TVS), or volatile dissolved solids (VDS).
- This method may also be used to determine nonvolatile (fixed) suspended solids (NVSS), total fixed solids (TFS), or fixed dissolved solids (FDS).
- Volatile and Nonvolatile suspended and fixed solids with the following relationships to other solids:

TS=TSS + TDS in water samples

TSS=VSS + NVSS in water samples

TDS=VDS + FDS in water samples

TS=TVS + TFS in water samples

% Solids=TVS + TFS in solid samples

Introduction and definitions:

- **Total Suspended Solids (TSS)**

Those solids, which are retained by a glass fiber, filter and dried to constant weight at 103-105ºC. Residue, non-filterable is an equivalent term.

- **Method Blank:**

A sample of laboratory pure water containing no target analyte that is taken through the entire sampling and analytical procedure. In this case, distilled water is used as the blank. The analysis of a method blank helps identifies any contamination introduced in the analysis process.

- **Laboratory Pure Water**

Reagent water meeting purity characteristics of ASTM Type II laboratory distilled water (daily conductivity <1.0µmhos/cm).

- **Duplicate sample**

Select routine samples to be analyzed twice. Independently prepare and analyze duplicate samples.

- **Laboratory fortified blank (LFB)**

Sample with known concentration of analyte that is used to asses the performance of total analytic system

- **VSS**

The suspended organic fraction, which will oxidize and will driven off as gas at temperature 550 ^{o}C $\pm$ 50 ^{o}C.

- **NVSS**

Are those solids that remain on the filter after ignition in a muffle furnace at 500-550oC

- **VDS**

Are those solids dissolved in a sample that pass through a glass fiber filter, are dried to a constant weight at 180,,aC, and are then lost through ignition in a muffle furnace at (500-550)^{o} C.

- **FDS**

Are those solids that remain after ignition in a muffle furnace at 500-550,,aC

- **TVS**

Or organic material, are the solids that are removed from a sample by ignition in a muffle furnace at 500-550oC

- **TFS**

Also known as total fixed solids or ash, are the solids that remain after ignition of the sample in a muffle furnace at 500-550 o C

Interferences:

- Negative errors in the volatile solids may be produced by loss of volatile matter during drying. Determination of low concentrations of volatile solids in the presence of high fixed solids concentrations may be subject to considerable error. In such cases, measure for suspect volatile components by another test, for example, total organic carbon. Highly alkaline residues may react with silica in sample or silica-containing crucibles.

Hazard and Precaution

NA

chemical and reagent:

Laboratory fortified blank:

(TS/TVS/TFS standard, 300/134/166 mg/L (LCS/LCSD **)**

- Ignite about 0.5 grams of NaCl at 550oC in a muffle furnace for 20 minutes, cool and store in a desiccator until needed.

- Dry 1 gram of KHP at 104±1 ^{o}C in an oven for one hour, cool and store in a desiccator until needed.

- Weigh 0.1000 g of dried NaCl and 0.2000 g of prepared KHP and dissolve in about 800 mL DI water in a 1L volumetric flask. Dilute to volume. Standard is ready for analysis.

Equipment and Supplies

- **Equipment:**

  - Filtration apparatus:
    One of the following, suitable for the filter disk selected

  - Membrane filter funnel.
    - Gooch crucible, 25-mL to 40-mL capacity, with Gooch crucible adapter.
    - Filtration apparatus with reservoir and coarse (40- to 60-m) fritted disk as filter support. Suction flask, of sufficient capacity for sample size selected
    - Drying oven controlled at 103 to 105°C
    - Muffle furnace for operation at 550°C.
    - Analytical balance capable of weighing to 0.1mg.
    - Thermometer
    - Magnetic stirrer with TFE stirring bar.

- **Glassware:**

- Wash bottle for distilled water
- Desiccator, provided with a desiccant containing a color indicator of moisture concentration or an instrumental indicator.
- Graduated cylinder, 25, 50,100, 250, 500 and 1,000ml.
- volumetric flasks 1000ml and 2000ml.
- Low-form beaker (Class B or better.)
- Pestle and Mortar
- Aluminum weighing dishes
- Watch Glass
- Forceps

- Glass-fiber filter disks without organic binder.
- Evaporating dishes: Dishes of 100-mL capacity made of
- one of the following materials:

Safety:

- **Safety tools**

Due to various hazards in the laboratory, safety glasses must be worn at all times. Be careful when using the oven at elevated temperatures to avoid burns. Use the tongs to remove the evaporating dish/crucible from the oven

- **Waste Disposal**

Dispose of sample waste down the drain with copious amounts of water

Sampling:

- **Sample Storage**

Measurement	Minimum Sample Size mL	Container	Sample Type	Preservation	Maximum Storage Recommended
Solid	200	P, G	c	Cool<=6°C	7 d

- **Sample handling**

The samples obtained from the sampling coordinator and after check by the lab staff

Procedure:

- Ignite residue produced by Method (2540 B. Total Solids Dried at 103–105°C, 2540 C. Total Dissolved Solids Dried at 180°C, or 2540 D)
- Total Suspended Solids Dried at 103–105°C) to constant weight in a muffle furnace at a temperature of 550°C.
- Ignite a blank glass fiber filter along with samples.
- Have furnace up to temperature before inserting sample. Usually, 15 to 20 min
- Ignition are required for 200 mg residue. However, more than one sample and/or heavier residues may overtax the furnace and necessitate longer ignition times.
- Let dish or filter disk cool partially in air until most of the heat has been dissipated.
- Transfer to a desiccator for final cooling in a dry atmosphere.
- Do not overload desiccator. Weigh dish or disk as soon as it has cooled to balance temperature.

- Repeat cycle of igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight, change is less than 4% or 0.5 mg, whichever is less.
- Weight loss of the blank filter is an indication of unsuitability of a particular brand or type of filter for this analysis.
- **Data Analysis and Calculations:**

Calculations:

mg volatile solids/L = ((A- B) * 1000)/ Sample volume, mL)

mg fixed solids/L = ((B - C) *1000) / Sample volume, mL)

where:

A = weight of residue + dish before ignition, mg,

B = weight of residue+ dish or filter after ignition, mg, and

C= weight of dish or filter, mg.

LFB recovery:

(Cb / I) * 100 =Recovery LFB

where:

Cb = LFB concentration determined experimentally

I = initial concentration from analytes added to LFB.

Relative percent difference:

$((D1 - D2)/((D1 + D2)/ 2))*100 = \%RPD$

where:

D1 = concentration determined for first duplicate, and

D2 = concentration determined for second duplicate

- **Quality Control:**

QC for method	frequency	Acceptance Criteria	Corrective Action:
Duplicates of the sample	at least 10% of all samples	within 5% of their average weight	If There is not extra sample for reanalysis or holding time expired " the sample must be reported as No result)"

Reporting Results:

NA

3-5 Settleable Solids

Introduction and Definitions:

- Settleable solids" is the term applied to the material settling out of suspension within a defined period. It may include floating material, depending on the technique

principle:

- This method is taken from The Standard Methods for the Examination of Water and Wastewater AWWA 23TH edition (2540 F. Settleable Solids).
- This procedure is suitable for the analysis of sewage, industrial effluent and river water samples.
- Settleable solids in surface and saline waters as well as domestic and industrial wastes may be determined and reported on either a volume (mL/L) or a weight (mg/L) basis
- A volume of water is put into Imhoff cone and allowed to set for a period time.
- the about of settleable solids is determined using the graduation on the cone.

Interferences:
NA

Hazard and Precaution:
NA

Chemicals and Reagents:
NA

Equipment and Supplies

Equipment:

- Filtration apparatus:

One of the following, suitable for the filter disk selected:

- Membrane filter funnel.
- Gooch crucible, 25-mL to 40-mL capacity, with Gooch crucible adapter.
- Filtration apparatus with reservoir and coarse (40- to 60-m) fritted disk as filter support.
- Suction flask, of sufficient capacity for sample size selected

- Drying oven controlled at 103 to 105°C
- Analytical balance capable of weighing to 0.1mg.
- Thermometer
- Magnetic stirrer with TFE stirring bar.

Glassware:

- Wash bottle for distilled water
- Imhoff cone

- glass vessel with a minimum diameter of 9 cm
- Desiccator, provided with a desiccant containing a color indicator of moisture concentration or an instrumental indicator.
- Graduated cylinder, 25, 50,100, 250, 500 and 1,000ml.
- Volumetric flasks 1000ml and 2000ml.
- Low-form beaker (Class B or better)
- Pestle and Mortar
- Aluminum weighing dishes
- Forceps
- Glass-fiber filter disks without organic binder.
- Evaporating dishes: Dishes of 100-mL capacity made of
- one of the following materials:

Safety:

Safety tools

Due to various hazards in the laboratory, safety glasses must be worn at all times.

Waste Disposal

Dispose of sample waste down the drain with copious amounts of water

Sampling:

Sample Storage

Measurement	Minimum Sample Size mL	Container	Sample Type	Preservation	Maximum Storage Recommended
Solid	200	P, G	c	Cool<=6°C	7 d

Sample handling

The samples obtained from the sampling coordinator and after check by the lab staff

Procedure:

Volumetric:

- Fill an Imhoff cone to the 1-L mark with a
- Well-mixed sample. Settle for 45 min, gently agitate sample near
- the sides of the cone with a rod or by spinning, settle 15 min

- Longer and record volume of settleable solids in the cone as milliliters per liter.
- If the settled matter contains pockets of liquid between large settled particles, estimate volume of these and subtract from volume of settled solids.
- The practical lower limit of measurement depends on sample composition and generally is in the range of 0.1 to 1.0 mL/L.
- Where a separation of settleable and floating materials occurs, do not estimate the floating material
- As settleable matter. Replicates usually are not required.
- Determine total suspended solids as in 2540D.
- Pour a well-mixed sample into a glass vessel of not less than 9 cm diam using not less than 1 L and sufficient sample to give a depth of 20 cm.
- Alternatively use a glass vessel of greater diameter and a larger volume of sample.
- Let stand 1 h and, without disturbing the settled or floating material, siphon 250 mL from center of container at a point halfway between the surface of the settled material and the liquid surface.
- Determine total suspended solids (milligrams per liter) of this supernatant liquor (2540D). These are the non-settleable solids.

Data Analysis and Calculations:

- **Calculations:**

mg settleable solids/L= (mg total suspended solids/L - mg non-settleable solids/L)

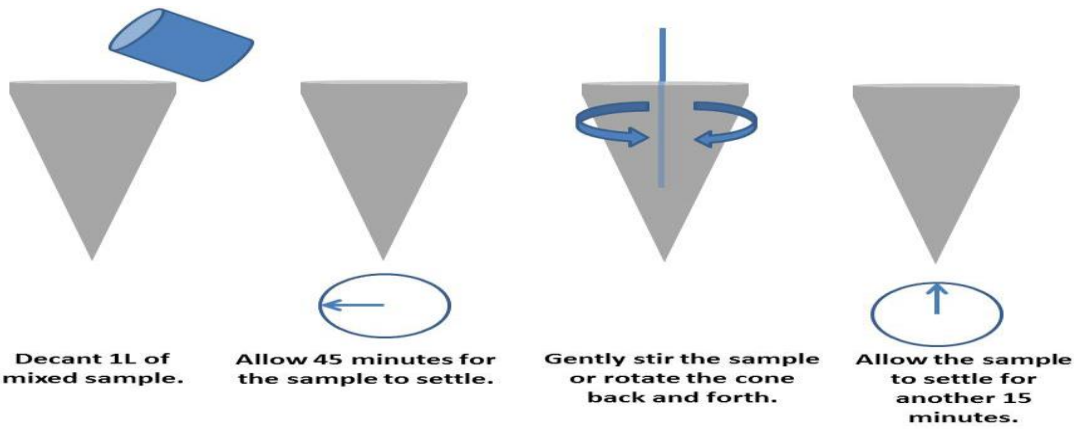
- **Quality Control:**

NA

Reporting:

NA

Flow chart:



4- Settled Sludge Volume (SV30)

Principal

a 30-min settled sludge volume or the ratio of the 15min to the 30min settled sludge volume has been used to determine the returned-sludge flow rate and when to waste sludge. The 30min settled sludge volume also is used to determine sludge volume index1 This method is inappropriate for dilute sludge because of the small volume of settled material. In such cases, use the volumetric test for settleable solids using an Imhoff cone.

Scope

The settled sludge volume of a biological suspension is useful in routine monitoring of biological processes. For activated sludge plant control

Equipment and apparatus:

Apparatus

- Settling column: Use 1L graduated cylinder equipped with a stirring mechanism consisting of one or more thin rods extending the length of the column and positioned within two rod diameters of the cylinder wall. Provide a stirrer able to rotate the stirring rods at no greater than 4 rpm (peripheral tip speed of approximately 1.3 cm/s).
- Stopwatch.
- Thermometer

Procedure

- Place 1.0 L sample in settling column and distribute solids by covering the top and inverting cylinder three times.
- Insert stirring rods, activate stirring mechanism, start the stop watch, and let suspension settle.
- Continue stirring throughout test.
- Maintain suspension temperature during test at that in the basin from which the sample was taken.
- Determine volume occupied by suspension at measured time intervals, e.g., 5, 10, 15,20, 30, 45, and 60 min.
- Report settled sludge volume of the suspension in milliliters for an indicated time interval.
- Variations in suspension temperature, sampling and agitation methods, dimensions of settling column, and time between sampling and start of the determination significantly affect results.
- Precision and Bias is not applicable.
- The precision for this test has not been determined.

5- Sludge volume index (SVI)

Principal

Clarifier performance & effluent quality depend directly on sludge settling and thickening characteristics, A measure of the sludge quality is the sludge volume index or SVI test.

SVI is the volume in ml occupied by one gram of MLSS after 30 minutes settling.

Scope

Wastewater aeration tank (mixed liquor)

Procedure

- Pour the well shaken sample into the settling column up to 50 ml mark and distribute solids inverting column 3 times.
- Insert stirring rods, activate stirring mechanism and let suspension settle.
- Continue stirring throughout test, maintain suspension temperature during test at that in the sludge basin from which the sample was taken.
- Determine the volume occupied by the suspension after 30 minutes and report as SSV.
- Determine the suspended solids concentration for the suspension and report as MLSS in g/L.
- The individual SSV (ml/1000 ml) is calculated by dividing the volume of sludge after 30 min. by the volume taken for analysis then multiply by 1000.

Data Analysis and Calculations:

- **Calculations:**

$$\text{SVI} = \frac{\text{volume of sludge after 30 min.in ml.}}{\text{mlss (mg\l)}} \times 1000$$

Organic analysis:

1- Chlorine residual by DPD

introduction

The Chlorination of wastewater is used to improve the quality of treated wastewater resulting from the wastewater treatment plants according to Egyptian Environmental low, NO 92 \2013, this low recorded that residual chlorine must be between 0.50 mg\ l to 1.0 mg\l.

this limits this ensure that the total coliform in treated wastewater.

Factors affects the residual chlorine depends on the content of ammonia, iron, manganese and some organic substances.

Under certain conditions some of the chlorine which reacts with ammonia is still available as a disinfectant and is commonly referred to as the "Combined Chlorine Residual".

The "Total Chlorine Residual is made up of Free Chlorine plus Combined Chlorine.

Chlorine in water is not stable and begins to decompose almost as soon it is injected, so it is important that chlorine residuals are measured immediately after the samples have been taken.

Interferences

- Concentrations of free chlorine greater than 4 ppm led to disappearing or fading of the red color as soon as it is formed.
- For concentrations of chlorine greater than 4 ppm, the sample must be diluted with chlorine-demand-free water.

Scope

This procedure describes how to measure Residual Chlorine in wastewater with DPD method for Out let of wastewater treatment plant.

Chemicals and Reagent

- **DPD tablets:**
  - DPD No 1 tablets for "Free Chlorine Residual".
  - DPD No 4 tablets for "Total Chlorine Residual".
  - DPD No 1 plus No 3 tablets for "Total Chlorine Residual".
  - 100 mg/l chlorine waterscape
- **Phosphate buffer solution:**
  - Dissolve 24 g anhydrous Na_2HPO_4 and 46 g anhydrous KH_2PO_4 in distilled water.
  - Combine with 100 mL distilled water in which 800 mg di sodium ethylenediamine tetraacetate dihydrate (EDTA) have been dissolved.

- Dilute to 1 L with distilled water and optionally add either 20 mg $HgCl_2$ or 2 drops toluene to prevent mold growth.
- Interference from trace amounts of iodide in the reagents can be negated by optional addition of 20 mg $HgCl_2$ to the solution.
- **CAUTION: $HgCl_2$ is toxic—take care to avoid ingestion.**

- **N,N-Diethyl-p-phenylenediamine (DPD) indicator solution:**
  - Dissolve 1 g DPD oxalate, or 1.5 g DPD sulfate pentahydrate, or 1.1 g anhydrous DPD sulfate in chlorine-free distilled water containing 8 mL H_2SO_4 and 200 mg disodium EDTA.
  - Make up to 1 L, store in a brown glass-stoppered bottle in the dark, and discard when discolored.
  - Periodically check solution blank for absorbance and discard when absorbance at 515 nm exceeds 0.002/cm. (The buffer and indicator sulfate are available commercially as a combined reagent in stable powder form.)
  - **CAUTION: The oxalate is toxic—take care to avoid ingestion**
- **Potassium permanganate solutions—Prepare a stock solution**
  - Containing 891 mg $KMnO_4$/1000 mL.
  - Dilute 10.00 mL stock solution to 100 mL with distilled water in a volumetric flask. When 1 mL of this solution is diluted to 100 mL with distilled water, a chlorine equivalent of 1.00 mg/L will be produced in the DPD reaction.

Sampling

Chlorine residual determinations must be carried out immediately (within 10 to 15 minutes) after sample collection due to the instability of chlorine.

Equipment and apparatus

- Colorimetric comparator, discs, and test vessels.

Procedure

- **Free Chlorine:**
  - Fill the test vessel in the left-hand compartment with approximately 10 mL of water sample.
  - Rinse out the vessel in the right-hand compartment with sample and leave in a few drops.
  - Add a DPD No. l tablet and crush with a stirring rod.
  - Fill to 10 mL with the sample and mix, then place the vessel in the right-hand compartment.

- Rotate the disc until the color of the sample is matched by one of the glass standards.
- Read immediately the value expressed in ppm from the indicator window. This is value "A".

- **Total Chlorine:**
  - To the colored sample above, add a DPD No. 3 tablet, mix to dissolve and allow to stand for 2 minutes.
  - Rotate the disc until the color of the sample is matched by one of the glass standards.
  - Read immediately the value expressed in ppm from the indicator window. This is value "B".
- **CAUTION: Analysis for free chlorine: Reading shall be taken immediately upon addition of DPD to avoid change in color.**

- **Data Analysis and Calculations:**

Calculations:

- Free Chlorine Residual = A in ppm
- Total Chlorine Residual = B in ppm
- Combined Chlorine Residual = (B - A) in ppm

Quality control:

- Results can be controlled by analyzing a duplicate sample.

Reporting

NA

2- Chlorides

Principal

Chloride, in the form of chloride (Cl^-), is one of the major inorganic anions in wastewater. High chloride content may harm metallic pipes and structures, as well as growing plants.

Scope

This procedure explains measuring Chloride in water and wastewater

Chemical and Reagent

- **Silver Nitrate 0.0141N, Solution:**
  - Weigh accurately using a weighing boat, 1.1975 g of silver nitrate AR.
  - Transfer quantitatively using a stream of distilled water, through a glass funnel, to a 500 ml volumetric flask.
  - Add sufficient distilled water to fill the flask to about ¾ full.
  - Inset stopper, invert and rotate the flask to dissolve the crystals.
  - Make up to the mark with distilled water.
  - Transfer the solution carefully, using a funnel, to a labeled bottle.
  - This solution is stable for 1 Month, mark with the expiry date.
- **Standard Chloride 0.0141N, Solution:**
  - Place about 1 g of sodium chloride for about 12 hours in an oven at 105 °C.
  - Weigh accurately 0.4120 g of the dried sodium chloride AR.
  - Transfer quantitatively using a stream of distilled water, through a glass funnel, to a 500 ml volumetric flask.
  - Add sufficient distilled water to fill the flask to about ¾ full.
  - Inset stopper, invert and rotate the flask to dissolve the crystals.
  - Make up to the mark with distilled water.
  - Transfer the solution carefully, using a funnel, to a labeled bottle.
  - This solution is stable for 1 Month, mark with the expiry date.
- **Potassium Chromate Solution 5 % w/v**
  - Weigh about 5 g of potassium chromate.
  - Transfer using a stream of distilled water, through a glass funnel, to a 100 ml volumetric flask.
  - Make up to the mark. Swirl to mix.
  - Transfer the solution to a 250 ml beaker and add drop wise 0.0141N $AgNO_3$ solution until a red precipitate is formed and mix well.
  - Allow to stand for about 12 hours and then decant off the clear solution.

- Filter through a qualitative grade filter circle.
- Transfer the filtered solution, using a funnel, to a labeled bottle.
- This solution is stable for 3 Months, mark with the expiry date.

Equipment and apparatus:

- analytical balance capable of measuring to 0.1 mg.
- Magnetic stirrer.
- Oven (set at 140°C).
- Erlenmeyer flask 250 ml.
- Volumetric flasks 500 ml.
- Burette, 25 ml, grade A.
- Pipette, volumetric, 25 ml, grade A.
- Pipette, volumetric, other sizes as required, grade A.
- Pipette filler
- Weighing boat.
- Glass funnels.
- Reagent bottles.

Procedures

- **Standardization of silver nitrate solution**

Before analysis carry out a standardization of the silver nitrate solution as follows:

- Take by volumetric pipette, 25 ml of NaCl solution and transfer to a 250 ml Erlenmeyer flask.
- Dilute the standard solution to approximately 100 ml with distilled water.
- Add 1 ml of potassium chromate solution.
- Add the silver nitrate titrant from a 25 ml burette slowly, stirring the sample continuously, to a pink/yellow end-point.
- Record the titer and volume of standard NaCl solution volume taken, on the chloride work sheet.
- Calculation of normality of silver nitrate solution:

$$\text{Normality of silver nitrate solution} = \frac{N \times V_1}{V_2}$$

Where:

N = normality of NaCl
V_1 = ml taken from NaCl
V_2 = ml titration from silver nitrate

- **Analysis of Sample**
  - A blank determination mist be carried out will each batch of samples.
  - Carry out a blank determination by using 100 ml of distilled water in place of sample record the on the chloride working sheet.
  - A quality control standard must be run with each batch of samples.
  - Directly titrate samples in the pH range 7 to 10 adjust samples to pH 7 to 10 with H2SO4 or NaOH if it is not in this range.
  - Do not uses a chloride type pH electrode or only use a portion of the sample to determine the amount of acid or alkali to use discard this portion of the sample.
  - Take by pipette, 25 ml of sample (or a volume that will give a titer between say 5 ml and 25 ml) and transfer to a 2500 ml Erlenmeyer flask.
  - Dilute the sample to approximately 100 ml with distilled water.
  - Add 1 ml of potassium chromate solution.
  - Add the silver nitrate titrant from the burette slowly, stirring the sample continuously, to a pink/yellow end-point.
  - Record the titer and standard NaCl solution volume taken, on the chloride work sheet.
  - Report for all samples, the blank and QC standard.

- **Data Analysis and Calculations:**
  Calculations:

The computer will automatically calculate the chloride concentration if you need to calculate if manuals use the following equation:

$$\text{mg Cl / L} = \frac{(\text{A} - \text{B}) \times \text{N} \times 35.450}{\text{ml of sample}}$$

Where:

A = ml titration for sample

B = ml titration for blank, and

N = Normality of $Ag\,NO_3$

$$\text{mg NaCl/L} = (\text{mg } CL^- / \text{L}) \times 1.65$$

Reporting Results

If the quality check meets the requirement then report the results.

- All results must be reported to 1 decimal place.
- If any of the results are less than 1 mg/L, report the result as “less than 1 mg/L or (> 1 mg/L).
- Enter all data from the chloride work sheet into the chloride spread sheet on the computer.
- Save the spread sheet and print out the chloride report sheet. Pass to the senior scientist or Laboratory Manager to sign off.

3- pH

Principal

The pH value of water or wastewater is the measurement of its acidity or alkalinity. It defined as the negative logarithmic of hydrogen ions in water or wastewater. A scale of 1 to 14 is used. for measurement, with 1 being extremely acidic and 14 being extremely alkaline. The midpoint (7.0) is neutral.

Importance of detecting pH value: The efficiency of chlorination and coagulation, and the corrosively of treated water, depend on pH. Monitoring of pH can indicate changes in raw and finished water quality.

Interferences

- The pH should be measured as soon as possible after sample collection, preferably within 15 minutes.
- Sample storage: If the sample must be stored, it should be refrigerated at 4 ^{o}C with NO preservatives added and the test performed no later than 6 hours after collection.
- Samples may be collected in glass or plastic containers, with a volume of at least 25 ml.

Scope

wastewater specially inlet and outlet plant

Chemical and Reagents

Calibrate the electrode system against standard buffer solutions of known pH usually 4.0, 7.0, 10.0.

Equipment and Apparatus

- pH meter and magnetic stirrer.
- pH meter consisting of potentiometer, glass electrode, reference electrode, and a temperature-compensating device.

Procedures

Calibration (General Instructions; for specific details see manufacturer's instructions):

- Remove electrode from storage solution rinse, dry with soft tissue.
- Place in initial buffer solution and set the lowest pH point (4.0).
- Remove electrode from the first buffer, rinse thoroughly with distilled water, blot dry.
- Place in second buffer and set the mid pH point (7.0).
- Remove electrode from the second buffer, rinse thoroughly with distilled water, blot dry.

- Place in third buffer and set the high pH point (10.0).
- Remove electrode from the second buffer, rinse thoroughly with distilled water, blot dry.
- Note: The pH reading of the buffer solutions should be within 0.1 pH units of the buffer pH.

Sample Analysis:

- Place the electrode in the water sample.
- Stir sample gently to ensure homogeneity.
- Read the pH value directly from the meter.

Reporting Results

- Report the pH of the raw wastewater, each stage of the treatment process, and the treated water at least once per day in the Daily Log Book.

4- Temperature

Principal

Temperature considered an important value in water and wastewater systems. In wastewater treatment systems specially in the activated sludge process temperature has a direct relation to the dissolved oxygen concentration. Elevated temperatures resulting from discharges of heated water from industrial plants may have significant ecological impact.

Interference

temperature value must be taken immediately whilst the sample is still in the sample jug.

Scope

Water and wastewater samples

Equipment and Apparatus

- Mercury thermometer with a scale marked in 1 ºC increment.
- The scale range for water samples should be in the (–10 to 110 ºC) Ideally the thermometer should have a calibration certificate.

Procedures

Pre analysis checks:

On site temperature measurements

- the temperature is to be taken on site during normal sampling refer to the laboratory procedure SP_L_01 After taking a sample, the temperature must be taken immediately whilst the sample is still in the sample jug.
- Wait until the mercury in the steam of the thermometer reaches a stable reading (approx.1 minute).
- Record the result to the nearest 0.5 ºC in the temperature.
- Temperature measurements in the laboratory: General laboratory operations e.g., temperature of a water bath
- Place a distilled water rinsed thermometer in the sample to be measured fix if necessary, with a support stand and clamp.
- Position yourself so that your eye is level with the meniscus of the mercury column.

Reporting Results

- Report sample temperature direct after mercury level stable raise. Enter all data from the temperature work sheet into the temperature spread sheet on the computer.
- Save the spread sheet and print out the temperature report sheet. Pass to the Senior Scientist or Laboratory Manager to sign off.

5- Ammonia

Introduction

In wastewaters the forms of nitrogen of greatest interest are, in order of decreasing oxidation state, nitrate, nitrite, ammonia, and organic nitrogen.

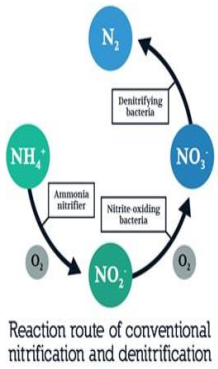
Organic nitrogen is defined functionally as organically bound nitrogen in the tri negative oxidation state, and vary from a few hundred micrograms per liter in some lakes to more than 20 mg/L in raw sewage.

Organic nitrogen and ammonia can be determined together and have been referred to as ‘‘kjeldahl nitrogen,’’ a term that reflects the technique used in their determination.

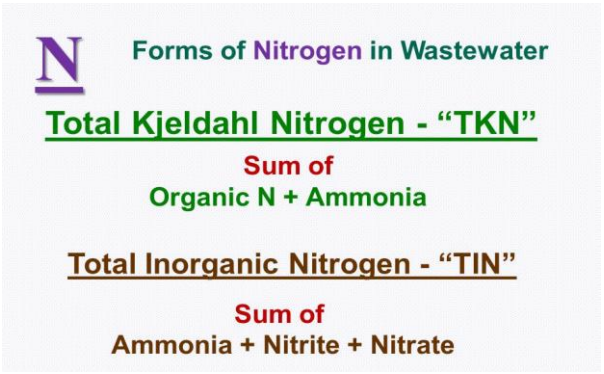
Total oxidized nitrogen is the sum of nitrate and nitrite nitrogen.

Nitrate is found only in small amounts in fresh domestic wastewater but in the effluent of nitrifying biological treatment plants nitrate may be found in concentrations of up to 30 mg nitrate as nitrogen/ L.

Ammonia concentrations encountered in water vary from less than 10 µg ammonia nitrogen /L in some natural surface and ground waters to more than 30 mg/L in some wastewaters.



Reaction route of conventional nitrification and denitrification



It is produced largely by deamination of organic nitrogen containing compounds and by hydrolysis of urea. At some water treatment plants, ammonia is added to react with chlorine to form combined chlorine residual.

Principles

The ammonia-selective electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an electrode internal solution of ammonium chloride. Dissolved ammonia (NH_3(aq) and NH_4) is converted to NH_3(aq) by raising pH to above 11 with a strong base. NH_3(aq) diffuses through the membrane and changes the internal solution pH that is sensed by a pH electrode.

Interference

Amines are a positive interference. This may be enhanced by acidification. Mercury and silver interfere by complexing with ammonia, unless the NaOH/EDTA solution is used.

Scope

Ammonia is measured in wastewater plants to determine the efficiency of treatment and occurred nitrification and / or denitrification. Ammonia is measured in influent and effluent.

This method is applicable to the measurement of 0.03 to 1400 mg NH_3-N/L in potable and surface waters and domestic and industrial wastes.

High concentrations of dissolved ions affect the measurement, but color and turbidity do not. Sample distillation is unnecessary.

Chemical and Reagents

- Water (Ammonia free water).
- Ammonia pH adjusting ISE
- NaOH 10 N. (Dissolve 400 gm NaOH in 1000 ml water)
- NaOH /EDTA soln 10 N. (Dissolve 400 gm NaOH in 800 ml water).
- Dissolve 45.2 g EDTA, tetra sodium salt tetra hydrate added to Stir to dissolve, cool, dilute to 1000 ml
- Stock ammonium chloride solution: Dissolve 3.819 gm anhydrous NH_4Cl; dried at 100 °C in water and dilute to 1000 ml (1000 mg/L).
- Standard ammonium chloride. (Preparation (0.1, 1, 10, 100,1000 mg NH_3-N/L)

Equipment and supplies

- ISE ammonia Meter
- Combination Ammonia
- Electrode Ammonia Electrode accessories
- Ammonia Electrode filling solution
- Ammonia Electrode storage solutions.
- Magnetic stirrer
- Stir bars
- Holder
- Volumetric pipettes
- Balance
- 100 ml conical flasks, 500, 200, 100 ml volumetric flasks.

Sampling

Most reliable results are obtained on fresh samples. If samples are to be analyzed within 24 h of collection, refrigerate unacidified at 4°C.

For preservation for up to 28 d, freeze at - 20°C unacidified, or preserve samples by acidifying to pH <2 and storing at 4°C.

Procedures

Preparation of standards:

- Prepare a series of standard solutions covering the concentrations of 1000, 100, 10, 1, and 0.1 mg NH_3-N/L by making decimal dilutions of stock NH_4Cl solution with water.

Electrometer calibration:

- Place 100 mL of each standard solution in a 150 mL beaker. Immerse electrode in standard of lowest concentration and mix with a magnetic stirrer. Limit stirring speed to minimize possible loss of ammonia from the solution.
- Maintain the same stirring rate and a temperature of about 25 °C throughout calibration and testing procedures.
- Add a sufficient volume of 10N NaOH solution (1 mL usually is sufficient) to raise pH above 11. If the presence of silver or mercury is possible, use NaOH/EDTA solution in place of NaOH solution.
- If it is necessary to add more than 1 mL of either NaOH or NaOH/EDTA solution, note volume used, because it is required for subsequent calculations. Keep electrode in solution until a stable millivolt reading is obtained.
- Do not add NaOH solution before immersing electrode, because ammonia may be lost from a basic solution.
- Repeat procedure with remaining standards, proceeding from lowest to highest concentration.
- Wait until the reading has stabilized (at least 2 to 3 min) before recording millivolts for standards and samples containing 1 mg NH_3-N/L.

Preparation of standard curve:

- Using semi logarithmic graph paper, plot ammonia concentration in mg NH3-N / liter on the log axis vs. potential in millivolts on the linear axis, starting with the lowest concentration at the bottom of the scale. If the electrode is functioning properly, a tenfold change of NH3-N concentration produces a potential change of about 59 mV.

Calibration of specific ion meter:

- Refer to manufacturer’s instructions and proceed as in above.

Measurement of samples:

- Dilute if necessary, to bring NH_3-N concentration to within calibration curve range.
- Place 100 mL sample in 150 mL beaker and follow procedure as in above.
- Record volume of 10N NaOH added.
- Read NH_3-N concentration from standard curve.

Calculations:

$$\text{mg } NH_3 - N/L = A \times B \times [(100 + D)/(100 + C)]$$

Where:

A: dilution factor,

B: concentration of NH_3-N/L, mg/L, from calibration curve,

C: volume of 10N NaOH added to calibration standards, mL,

D: volume of 10N NaOH added to sample, ml.

Quality control

- This standard must not be prepared by the analyst who prepared the calibration standards. Dissolve 2.359 g of anhydrous Ammonium Sulphate (dried at 100 ºC for One hour) in 1000 ml of distilled water.
- This is the 500 mg/L stock standard solution.
- This solution must be prepared monthly, mark with the expiry date
- Pipette 1ml of 500 mg/L stock solution into a 500 ml volumetric flask and dilute it to the mark using distilled water.
- This is the 1mg/L intermediate standard.
- This solution must be prepared daily.
- Pipette 60 ml of 1 mg/L intermediate standard into 200 ml volumetric flask and dilute it to the mark using distilled water
- This is the 0.3 mg/L Quality Control standard
- This solution must be prepared daily

Reporting Results

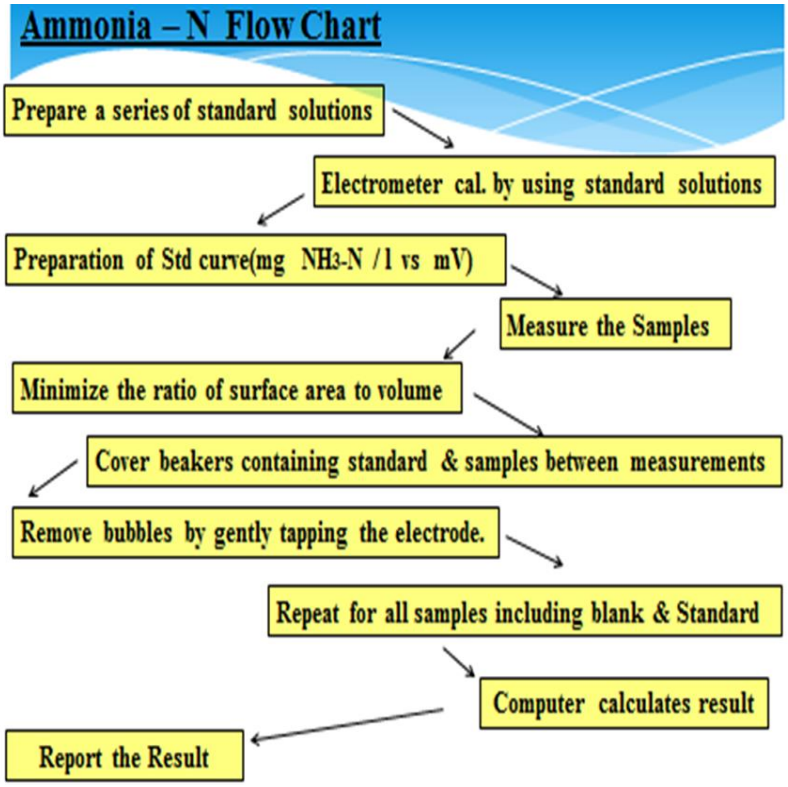
- All results must be reported to 2 decimal places.
- If any ammonia result is less than 3 µg NH_3-N/L, report the result as "< 3 µg NH_3-N/L".
- All results must be reported to 1 decimal place.
- Enter all data from the ammonia work sheet into the ammonia spread sheet on the computer.

- Save the spread sheet and print out the ammonia report sheet. Pass to the Senior Scientist or Laboratory Manager to sign off.

Note:

- Use beakers that minimize the ratio of surface area to volume.
- Keep beakers containing standard, and samples covered between measurements.
- After immersion in solution, check the electrode from any air bubbles on the membrane surface and remove bubbles by gently tapping the electrode.

Flow chart



Reference

This method is taken from standard methods for the examination of water and wastewater edition 22nd, 4500-D, 2011. "Ammonia Selective Electrode Method "

6- Nitrate NO_3

Introduction

Total oxidized nitrogen is the sum of nitrate and nitrite nitrogen. Nitrate is found only in small amounts in fresh domestic wastewater but in the effluent of nitrifying biological treatment plants nitrate may be found in concentrations of up to 30 mg nitrate as nitrogen/ L.

Principle

The NO^{3-}ion electrode is a selective sensor that develops a potential across a thin, porous, inert membrane that holds in place a water-immiscible liquid ion exchanger.

The electrode responds to NO^{3-} ion activity between about 10–5 and 10–1 M (0.14 to 1400 mg NO3–-N/L).

The lower limit of detection is determined by the small but finite solubility of the liquid ion exchanger.

Interference

- Chloride and bicarbonate ions interfere when their weight ratios to NO^3-N are 10 or 5, respectively.
- Ions that are potential interferences but do not normally occur at significant levels in potable waters are NO_2, CN, S_2, Br, I, ClO_3, and ClO_4.
- Although the electrodes function satisfactorily in buffers over the range pH 3 to 9, erratic responses have been noted where pH is not held constant.
- Because the electrode responds to NO_3 activity rather than concentration, ionic strength must be constant in all samples and standards.
- Minimize these problems by using a buffer solution containing Ag_2SO_4 to remove Cl, Br, I, S_2, and CN, sulfamic acid to remove NO_2, a buffer at pH 3 to eliminate HCO_3 and to maintain a constant pH and ionic strength, and $Al_2(SO_4)_3$ to complex organic acids.

Scope

Nitrate is indicated to nitrification and denitrification in wastewater plant, it is measure in effluent in wastewater plant.

Chemical reagents

Nitrate-free water.

Stock nitrate solution:

- Dry potassium nitrate (KNO_3) in an oven at 105 °C for 24 h.
- Dissolve 0.7218 g in water and dilute to 1000 mL; 1.00 mL = 100 µg NO_3^--N.
- Preserve with 2 ml $CHCl_3$/L. This solution is stable for at least 6 months.

Standard nitrate solutions:

- Dilute 1.0, 10-, and 50-ml stock nitrate solution to 100 ml with water to obtain standard solutions of 1.0, 10, and 50 mg NO_3^--N/L, respectively.

Buffer solution:

- Dissolve 17.32 g $Al_2(SO_4)_3.18H_2O$, 3.43 g Ag_2SO_4, 1.28 g H_3BO_3, and 2.52 g sulfamic acid (H_2NSO_3H), in about 800 mL water.
- Adjust to pH 3.0 by slowly adding 0.10N NaOH. Dilute to 1000 mL and store in a dark glass bottle.

Sodium hydroxide, NaOH, 0.1N.

Reference electrode filling solution:

- Dissolve 0.53 g $(NH_4)_2SO_4$ in water and dilute to 100 ml.

Equipment and Supplies

- pH meter, expanded-scale or digital, capable of 0.1 mV resolution.
- Double-junction reference electrode.
- Fill outer chamber with $(NH_4)_2SO_4$ solution.
- Nitrate ion electrode: Carefully follow manufacturer's instructions regarding care and storage.
- Magnetic stirrer: TFE-coated stirring bar.

Sampling

- Start NO^{3-} determinations promptly after sampling.
- If storage is necessary, store for up to 2 d at 4 °C; disinfected samples are stable much longer without acid preservation.
- For longer storage of unchlorinated samples, preserve with 2 ml conc. H_2SO_4/L and store at 4°C.
- **Note**: When sample is preserved with acid, NO^{3-} and NO^{2-} cannot be determined as individual species.

Procedures

Standardization of KMnO4 titrant solution

- Weigh 3 batches of 100 mg of anhydrous sodium oxalate into 400 ml beakers and dissolve each weight in 100 ml distilled water.
- Add 10 ml of (1+1) sulfuric acid and heat rapidly to 90-95 °C.
- Titrate with KMnO4 solution to a slight pink color end point. Repeat steps on the other two weights of sodium oxalate and a blank of distilled water.

$$\text{Normality of } KMnO_4 = \frac{Weight\ of\ Na_2C_2O_4}{(A - B) \times 0.335}$$

Where:

A = ml titrant for sample

B = ml titrant for blank

- Take the average of the three titrations.

Standardization of stock sodium nitrite solution:

- Pipette 50 ml of standard 0.01 M (0.05 N) KMnO4, 5 ml concentrated sulphuric acid and by submersing the pipette tip below the surface of permanganate acid solution add 50 ml of the stock nitrite solution into a glass stopper flask.
- Shake gently and warm to 70 to 80 °C on a hot plate.
- Remove the permanganate color by adding sufficient portions of 0.025 M standard sodium oxalate solution.

Titrate excess sodium oxalate with 0.01 M KMnO4 to the faint pink end point:

$$A = \frac{[(B \times C) - (D \times E) \times 7}{F}$$

Where:

A = mg NO_2-N content in stock nitrite solution

B = Total ml standard $KMnO_4$ used

C = Normality of standard $KMnO_4$

D = Total ml of standard $Na_2C_2O_4$ added

E = Normality of standard $Na_2C_2O_4$ added

F = ml of stock nitrite solution taken for titration

Quality control:

- Precision and Bias
- Over the range of the method, precision of ±0.4 mV, corresponding to 2.5% in concentration, is expected.

Reporting Resulting

- If the quality control standard result meets the requirements then report the results.
- All results must be reported to 2 decimal places.
- If any nitrate result is less than 1.4 µg NO_3-N/L, report the result as "< 1.4 µg NO_3-N/L".

- Save the spread sheet and print out the nitrate report sheet. Pass to the Senior Scientist or Laboratory Manager to sign off.
- When the nitrate report sheet has been signed off the daily report can be prepared.
- If all the quality checks meet the requirements then report the results.
- All results must be reported to 1 decimal place.
- Enter all data from the Nitrate-N work sheet into the Nitrate-N spread sheet on the computer.
- Save the spread sheet and print out the Nitrate-N report sheet. Pass to the Senior Scientist or Laboratory Manager to sign off.
- When the Nitrate-N report sheet has been signed off the daily report sheet can be prepared
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Flow chart

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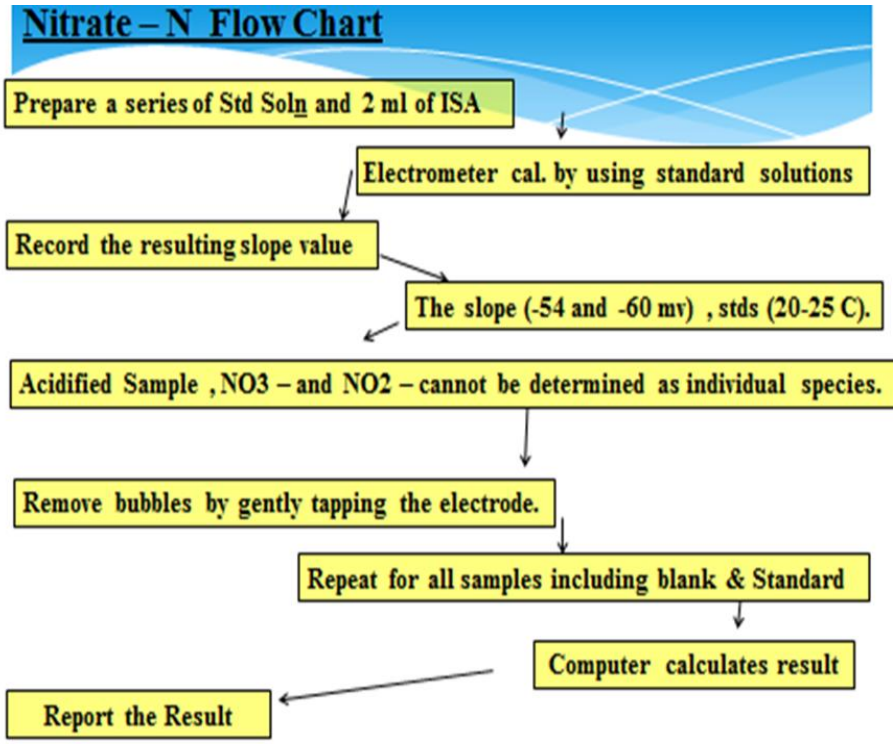


Reference

This Method is taken from "Standard Methods for the examination of water and wastewater 20th edition "4500-NO3–D. Nitrate Electrode Method "

7- Nitrite NO_2

Introduction

Total oxidized nitrogen is the sum of nitrate and nitrite nitrogen.

Nitrite is an intermediate oxidation state of nitrogen, both in the oxidation of ammonia to nitrate and in the reduction of nitrate. Such oxidation and reduction may occur in wastewater treatment plants, water distribution systems, and natural waters.

Principle

Nitrite measured in effluent in wastewater plant, Nitrite nitrogen seldom appears in concentrations greater than 1 mg/L, even in waste treatment plant effluents. Its concentration in surface and ground-water is normally much below 0.1 mg/L.

For this reason, sensitive colorimetric methods are needed for its measurements.

Nitrite is determined through formation of a reddish-purple azo dye that the nitrite ion as nitrous acid reacts with the amino group of sulfanilic acid in acidic conditions to form a diazonium salt which combines with N(1-naphthyl)–ethylenediamine dihydrochloride to form a bright-colored reddish purple azo dye.

The color produced is directly proportional to the amount of nitrite present in the sample.

Photometric measurements can be made in the range 5 to 50 µg N/L. Higher NO2- concentrations can be determined by diluting a sample.

The following ions interfere because of precipitation under test conditions and should be absent: Fe3+, Pb2+, Hg2+ and Ag+. Cupric ion may cause low results by catalyzing decomposition of the diazonium salt. Remove suspended solids by filtration.

Interference

- Chemical incompatibility makes it unlikely that NO_2^-, free chlorine, and nitrogen trichloride (NCl_3) will coexist. NCl_3 imparts a false red color when color reagent is added.
- The following ions interfere because of precipitation under test conditions and should be absent: Sb^3,Au^3, Bi^3, Fe^3, Pb^2, Hg^2, Ag , chloroplatinate ($PtCl_6^2$), and metavanadate (VO_3^2). Cupric ion may cause low results by catalyzing decomposition of the diazonium salt.
- Colored ions that alter the color system also should be absent.
- Remove suspended solids by filtration.

Scope

Make the determination on fresh samples to prevent bacterial conversion of NO^{2-} to NO^{3-} or NH_3.

Chemical and reagents

Water

Laboratory distilled water.

Color Reagent

- To 800 ml of distilled water add10 g of sulfanilamide and 100 ml 85% phosphoric acid.
- Stir the contents of the beaker with a glass rod until all the solids has dissolved.
- Add 1g of N-(1-naphthyl)–ethylenediamine dihydro-chloride and mix to dissolve.
- Dilute to 1 L with water and transfer the solution to a dark reagent bottle.
- Label the bottle “Color Reagent for Nitrite Determination”. Write your name, the date of preparation and the expiry date. This solution is stable for one month when stored in a dark bottle in refrigerator.

250 mg NO2-N/L stock sodium nitrite solution

- Dissolve 1.232 g of sodium nitrite (dried at 105 °C for 24 h) in water and dilute to 1000 ml in a volumetric flask. Add 1 ml of chloroform to preserve the stock solution.
- This solution is stable for one month.
- Mark with the date of preparation and the expiry date.
- This solution must be standardized before use.

50 mg NO2-N/L intermediate sodium nitrite solution:

- Pipette 50 ml of the stock solution into 250 ml volumetric flask and dilute to with water to the mark.
- This solution must be prepared daily.
- Mark with the date of preparation and the expiry date.

0.5 mg NO2-N/L standard sodium nitrite solutions:

- Pipette 10 ml of the intermediate solution into a 1L volumetric flask and dilute to with water to the mark.
- This solution must be prepared daily.
- Mark with the date of preparation and the expiry date.

Equipment and Supplies

- pH meter
- Colorimetric equipment HACH Spectrophotometer DR 2010
- 0.45 µm pore 47mm diameter filter
- 100, 250, 500, 1000 ml volumetric flasks

- Glass rod
- Volumetric pipettes
- 100 ml conical flasks
- Balance
- 50, 100 ml cylinders
- 25 ml burette
- 100, 400 ml beakers
- Magnetic stirrer & Hot plate
- Stirrer bars

Procedures

Standardization of KMnO4 titrant solution

- Weigh 3 batches of 100 mg of anhydrous sodium oxalate into 400 ml beakers and dissolve each weight in 100 ml distilled water.
- Add 10 ml of (1+1) sulfuric acid and heat rapidly to 90-95 °C.
- Titrate with $KMnO_4$ solution to a slight pink color end point.
- Repeat steps on the other two weights of sodium oxalate and a blank of distilled water.

$$\text{Normality of } KMnO_4 = \frac{Weight\ of\ Na_2C_2O_4}{(A - B) \times 0.335}$$

Where:

A = ml titrant for sample

B = ml titrant for blank

- Take the average of the three titrations.

Standardization of stock sodium nitrite solution:

- Pipette 50 ml of standard 0.01 M (0.05 N) $KMnO_4$, 5 ml concentrated sulphuric acid and by submersing the pipette tip below the surface of permanganate acid solution add 50 ml of the stock nitrite solution into a glass stopper flask.
- Shake gently and warm to 70 to 80 °C on a hot plate.
- Remove the permanganate colour by adding sufficient portions of 0.025 M standard sodium oxalate solution.

Titrate excess sodium oxalate with 0.01 M KMnO4 to the faint pink end point.

$$A = \frac{[(B \times C) - (D \times E) \times 7}{F}$$

Where:

A = mg NO_2-N content in stock nitrite solution

B = Total ml standard $KMnO_4$ used

C = Normality of standard $KMnO_4$

D = Total ml of standard $Na_2C_2O_4$ added

E = Normality of standard $Na_2C_2O_4$ added

F = ml of stock nitrite solution taken for titration

Quality control

- A Quality Control standard (QC) must be run with each batch of samples.
- The target concentration used is 0.2 mg NO_2-N/L.
- The QC must be prepared with reagents independent of the reagents used for calibration.
- The analyst, independent of the analyst who prepared the standards for calibration, must prepare the QC standard solution.

Use of control chart

- A "Shewert" Control chart has been set up using the standard solution at 0.2 mg NO_2-N/L as the target concentration. For a more detailed explanation of Quality Control charts and how they should be used refer to document "Quality Control Charts".
- Plot the result from the Quality Control Standard onto the control chart as soon as the result available.

Analysis of samples

- Preparation of calibration Carve.
- Turn on the spectrophotometer and allow 20 minutes to warm up before use.
- Close the sample chamber's lid and select a wavelength of 543 nm.
- Label six 100 ml volumetric flasks from 0 to 5.
- Pipette the required volume of intermediate sodium nitrite solution into each of the volumetric flasks according to next table.

Make the volumes of the solution in the volumetric flasks up to the mark with distilled water. Flask	Vol. of Nitrite Solution (ml)	Vol. of Distilled Water (ml)	Conc. Of Nitrite-N [(NO_2-)-N] (µg/L)
0	0	100	0
1	1	99	5
2	2	98	10
3	3	97	15
4	4	96	20
5	5	95	25

- Stopper the flasks and invert several times to ensure that the solution is well mixed.
- Label six 100 ml beakers from 0-5. One must be a Quality Control Standard.
- Pipette 50 ml of solution from volumetric flasks "0" into a 100 ml beaker "0".
- Add 2 ml of color reagent to solution in the beaker and mix with a glass rod.
- Repeat the instructions for the five remaining volumetric flasks.
- Allow all solutions to stand for a minimum of 10 minutes but no more than 2h before measuring absorbance
- Fill a cuvette with the solution from beaker "0". This is the blank.
- Clean the cuvette with a tissue and place in the cell holder in the sample chamber of the spectrophotometer.
- Select Absorbance using the mode keypad.
- Press the "Cal" keypad.
- The display will update to zero absorbance.
- Open the sample chamber's lid and remove the cuvette containing the blank solution.
- Measure the absorbance of each of the five remaining standard solution.
- Record the absorbance of the standard solutions on the laboratory sheet and plot the calibration curve.

Sample Measurement

- Filter about 70 ml of sample through a 0.45 µm pore 47mm diameter filter.
- Adjust the pH of the sample to within the range 5 and 9 with 1N HCl for higher pH or NH4OH for lower pH.

- Pipette 50 ml sample (or a portion diluted to 50 ml) and 50 ml of the Quality Control standard into two separate 100 ml beakers.
- Add 2 ml of color reagent to sample, QC standard and 50 ml of distilled water as a blank.
- Allow solutions to stand for a minimum 10 minutes but no more than 2 h before measuring the absorbance.
- Fill a cuvette with the blank solution.
- Clean the cuvette with a tissue and place in the cell holder in the sample chamber of the spectrophotometer.
- Press “Zero” to give zero absorbance for the blank.
- Read the absorbance for the sample and the QC standard and record on the laboratory sheet.
- Enter the data from the work sheet into the spread sheet of nitrite on the computer.
- Compute sample concentration directly from the calibration curve.

Quality Control Checks

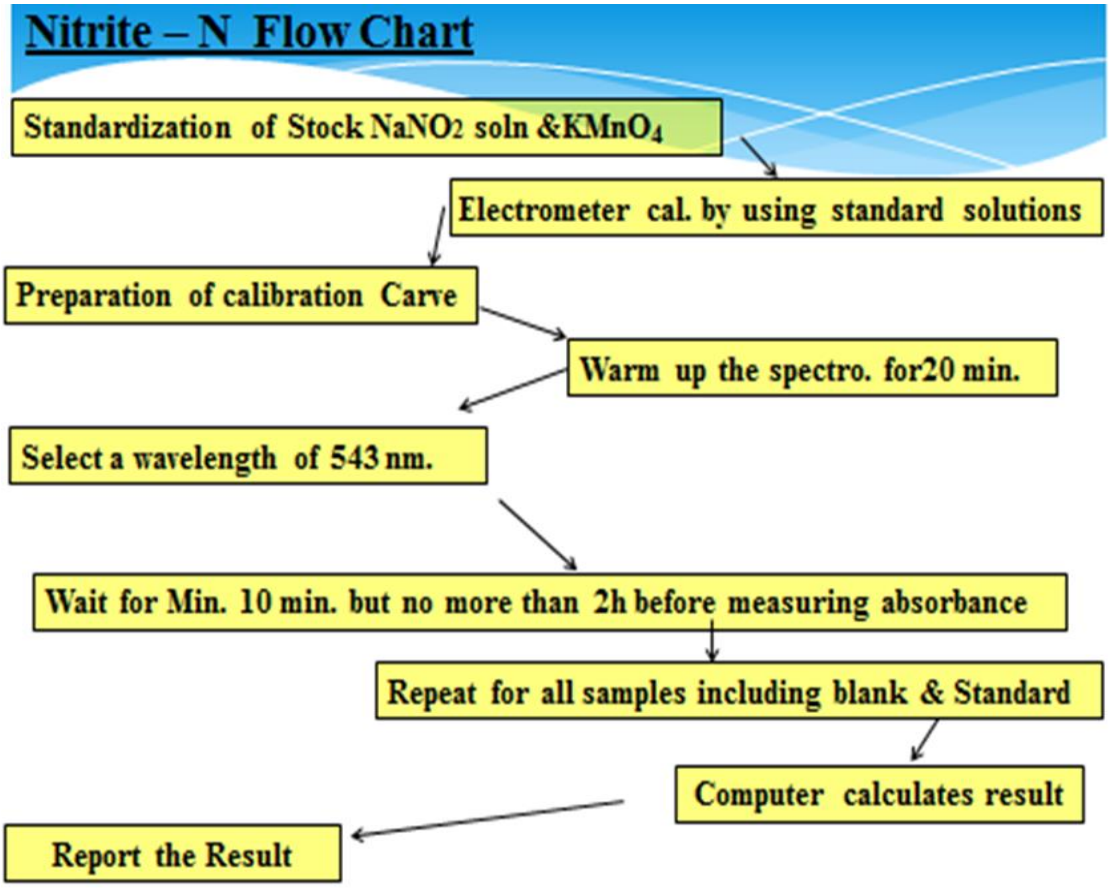
- Plot the quality control standard result on the quality control chart and check that the standard meets the quality requirements (detailed in SP_L_02 Quality Control Charts Laboratory Procedures)
- if the quality requirements are not met then report the failure to the Senior Scientist and Laboratory Manager.
- You must not report the results.

Reporting Results

- If the quality control standard result meets the requirements then report the results.
- All results must be reported to 2 decimal places.
- If any nitrite result is less than 5 µg NO_2-N/L, report the result as “< 5 µg NO_2-N/L”.
- Save the spread sheet and print out the nitrite report sheet. Pass to the Senior Scientist or Laboratory Manager to sign off.
- When the nitrite report sheet has been signed off the daily report can be prepared.
- If all the quality checks meet the requirements then report the results.
- All results must be reported to 1 decimal place.
- Enter all data from the Nitrite-N work sheet into the Nitrite-N spread sheet on the computer.

- Save the spread sheet and print out the Nitrite-N report sheet. Pass to the Senior Scientist or Laboratory Manager to sign off.
- When the Nitrite-N report sheet has been signed off the daily report sheet can be prepared.

Flow chart



Reference

This method is taken from Standard Methods for the Examination of water and wastewater edition 19:1995, 4500-B. "Nitrogen (Nitrite) Colorimetric Method"

8- Dissolved Oxygen (D.O)

Introduction

Dissolved oxygen can be defined as The amount of oxygen dissolved in water or waste water, and its levels in wastewaters depend on the physical, chemical, and biochemical activities in the water body.

Principle

Two methods for DO analysis are described, the Winkler or iodometric method and its modifications and the electrometric method using membrane electrodes.

The iodometric method is a titrimetric procedure

- The iodometric method is not suited for field testing and cannot be adapted easily for continuous monitoring or for D.O.
- determination in situ., and its modifications are subject to serious errors caused by interferences.
- based on the oxidizing property of DO
- Manganous sulfate react with potassium iodide in the presence of alkali to form white precipitate of manganous hydroxide, which subsequently oxidized by dissolved oxygen to form brown precipitate of manganic hydroxide.
- Manganic hydroxide dissolved by acidification and iodine liberates which is equivalent to the DO concentration.
- Iodine is titrated against standard sodium thiosulfate in the presence of starch as indicator

Membrane electrodes provide

- an excellent method for D.O. analysis in polluted or highly colored waters, and strong wastes, the oxygen permeable plastic membrane serves as a diffusion barrier against impurities.
- They used in analysis in situ they eliminate errors caused by sample handling and storage.
- the membrane electrode procedure is based on the rate of diffusion of molecular oxygen across a membrane.

Chemical and reagents

Manganous sulfate solution:

- Dissolve 480 g $MnSO_4$, $4H_2O$, 400 g $MnSO_4$. $2H_2O$, or 364 g $MnSO_4$, H_2O in distilled water, filter, and dilute to 1 L.

Alkali-iodide-azide reagent:

- Dissolve 500 g NaOH (or 700 g KOH) and 135 g NaI (or 150 g KI) in distilled water and dilute to 1 L.
- Add 10 g NaN_3 dissolved in40 mL distilled water.
- Potassium and sodium salts may be used interchangeably.

Sulfuric acid, H_2SO_4, conc.:

Starch:

- dissolve 2 g starch and 0.2 g salicylic acid, as a preservative, in 100 ml hot distilled water.

Standard sodium thiosulfate titrant:

- Dissolve 6.205 g$Na_2S_2O_3$.$5H_2O$ in distilled water.
- Add 1.5 mL 6N NaOH or 0.4 g solid NaOH and dilute to 1000 mL.
- Standardize with bi-iodate or dichromate

In dichromate method:

- Dissolve 1.226g $K_2Cr_2O_7$ in1000 mL to yield a 0. 0 25N solution,
- Store in a glass-stoppered bottle.
- -To 80 mL distilled water, add, with constant stirring, 1 mL concH_2SO_4 ,1mL 0.025 N K2Cr2O7, and 1 g KI.
- Titrate immediately with 0.025 N $Na_2S_2O_3 5H_2O$ until the yellow color of the liberated iodine almost is discharged.
- Add 1 mL starch indicator solution and continue titrating until the blue color disappears
- 1ml 0.025 N $K_2Cr_2O_7$ =1ml 0.025 N $Na_2S_2O_3$ $5.H_2O$

Equipment and Supplies

- DO meter and BOD Bottle 300ml.

Sampling

- To be collected in specific BOD bottle with 300 ml volume and stopper at the collection time (0.25 h) or add the precipitation reagents and liberation of iodine and titration to be carried out later on the lab. (8 h)

Procedures

- To the sample, add 1 mL $MnSO_4$ solution, followed by 1 mL alkali-iodide-azide reagent. add 1.0 mL conc H_2SO_4.
- mix by inverting several times until dissolution is complete.
- Titrate a volume corresponding to 200 mL original sample
- Titrate with 0.025M $Na_2S_2O_3$ solution to a pale straw color.
- Add a few drops of starch solution and continue titration to first disappearance of blue color

Calculation:

- For titration of 200 mL sample, 1 mL 0.025M $Na_2S_2O_3$= 1 mg DO/L.

Quality control:

QC for method	**frequency**	**Acceptance Criteria**	**Corrective Action:**
Zero check with zero oxygen sample	once per analysis batch	<0.2	R-prepare reagent and standard may indicate
Duplicates of the sample		%RPD within +_10%	May indicate the presence of toxic The batch sample must be reported as"NO result"

9- Total Phosphorus (TP)

Introduction

Phosphorus is essential to the growth of organisms the discharge of raw or treated wastewater, agricultural drainage, or certain industrial wastes to that water may stimulate the growth of photosynthetic aquatic micro- and macroorganisms., Phosphates also occur in bottom sediments and in biological sludges, both as precipitated inorganic forms and incorporated into organic compounds.

C:N:P ratio must be 100:5:1 for good growth of bacteria and good treatment of waste water. Total Phosphorus consists of orthophosphates, condensed phosphates (pyro-, meta-, and other polyphosphates), and organically bound phosphates.

Orthophosphates applied to agricultural or residential cultivated lands as fertilizers, condensed phosphates are major constituents of many commercial cleaning preparations and Organic phosphates are formed by body wastes and food residues.

Principle

Method: 4500-p-Persulfate digestion method for digestion and Vanadomolybdophosphoric acid colorimetric Method for determination.

Digestion methods: Persulfate Digestion Method

- Because phosphorus may occur in combination with organic matter, a digestion method to determine total phosphorus must be able to oxidize organic matter effectively to release phosphorus as orthophosphate.

Colorimetric method: The vanadomolybdophosphoric acid method

- It is most useful for routine analysis in the range of 1 to 20 mg P/L.
- In a dilute orthophosphate solution, ammonium molybdate reacts under acid conditions to form a heteropoly acid, molybdophosphoric acid.
- In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed.
- The intensity of the yellow color is proportional to phosphate concentration.

Interference

- Positive interference is caused by silica and arsenate only if the sample is heated.
- Negative interferences are caused by arsenate, fluoride, thorium, bismuth, sulfide, thiosulfate, thiocyanate, or excess molybdate.
- Blue color is caused by ferrous iron but this does not affect results if ferrous iron concentration is less than 100 mg/L.
- Sulfide interference may be removed by oxidation with bromine water
- If HNO_3 is used in the test, Cl_ interferes at 75 mg/L

Chemical and reagents

- Phenolphthalein indicator as an aqueous solution.
- Sulfuric acid solution: (Carefully add 300 mL conc H_2SO_4 to approximately 600 mL distilled water and dilute to 1 L with distilled water).
- Ammonium persulfate, $(NH_4)_2S_2O_8$, solid, or potassium persulfate, $K_2S_2O_8$, solid.
- Sodium hydroxide, NaOH, 1N.
- Phenolphthalein indicator aqueous solution.
- Hydrochloric acid, HCl, 1 + 1. H_2SO_4, $HClO_4$, or HNO_3 may be substituted for HCl. The acid concentration in the determination is not critical but a final sample concentration of 0.5N is recommended.
- Activated carbon to remove fine particles by rinsing with distilled water.
- Vanadate-molybdate reagent
  a- Solution A: Dissolve 25 g ammonium molybdate, $(NH_4)_6Mo_7O_24.4H_2O$, in 300 mL distilled water.
  b- Solution B: Dissolve 1.25 g ammonium metavanadate, $NH4VO_3$, by heating to boiling in 300 ml distilled water. Cool and add 330 ml conc HCl.
  c- Cool Solution B to room temperature, pour Solution A into Solution B, mix, and dilute to 1 L to obtain Vanadate-molybdate reagent:
- Standard phosphate stock solution

  Dissolve in distilled water 219.5 mg anhydrous KH_2PO_4 and dilute to 1000 ml; 1.00 ml = 50.0 µg PO_4.

Equipment and Supplies

Apparatus for digestion method

- Hot plate: A 30 × 50 cm heating surface is adequate.

Apparatus for Colorimetric method

One of the following is required:

- Spectrophotometer, for use at 400 to 490 nm.
- Filter photometer, provided with a blue or violet filter exhibiting maximum transmittance between 400 and 470 nm, A wavelength of 470 nm usually is used.

Sampling

- If total phosphorus is to be determined alone, add H_2SO_4 or HCl to pH<2 and cool to 4 °C, or freeze without any additions.
- In some cases, 40 mg $HgCl_2$/L may be added to the samples, especially when they are to be stored for long

- Do not store samples containing low concentrations of phosphorus in plastic bottles unless kept in a frozen state because phosphates may be adsorbed onto the walls of plastic bottles.
- Rinse all glass containers with hot dilute HCl, then rinse several times in reagent water.

CAUTION:

- $HgCl_2$ is a hazardous substance; take appropriate precautions in disposal; use of $HgCl_2$ is not encouraged.
- Do not add either acid or $CHCl_3$ as a preservative when phosphorus forms are to be determined.

Procedures

- 50 ml dilution+ 1 drop ph.ph, if pink color appears,
- add H_2SO_4 soln until pink color disappear
- Add 0.5 gm potassium per sulphate and boiling 20: 30 minutes until volume become 10 ml, Cool, complete to 30 ml dis.H_2O.

Sample PH adjustment:

- Add 1 drop ph.ph, Add NaOH(1N) to pink colour appear, Complete to 50 ml dis.H_2O.
- Neutralize pink colour by (1:1HCL)
- Complete to 100 ml dis.H_2O.

Colour removal from sample:

- Add 0.4 gm charcoal,
- Shake well, wait 5 minutes,
- take 35 ml from filtrate.

Colour development in sample:

- Add 10 ml Vanadate molybdate reagent and dilute to 50 ml dis.H_2O.
- Make blank (35 ml dis.H_2O. +10 ml Vanadate molybdate reagent and dilute to 50 ml dis.H_2O.
- Make calibration curve at 470 nm.

Calculation

$$\text{mg P/L} = \frac{\text{mg P (in 50 mL final volume)} \times 1000}{\text{mL sample}}$$

Precision and Bias

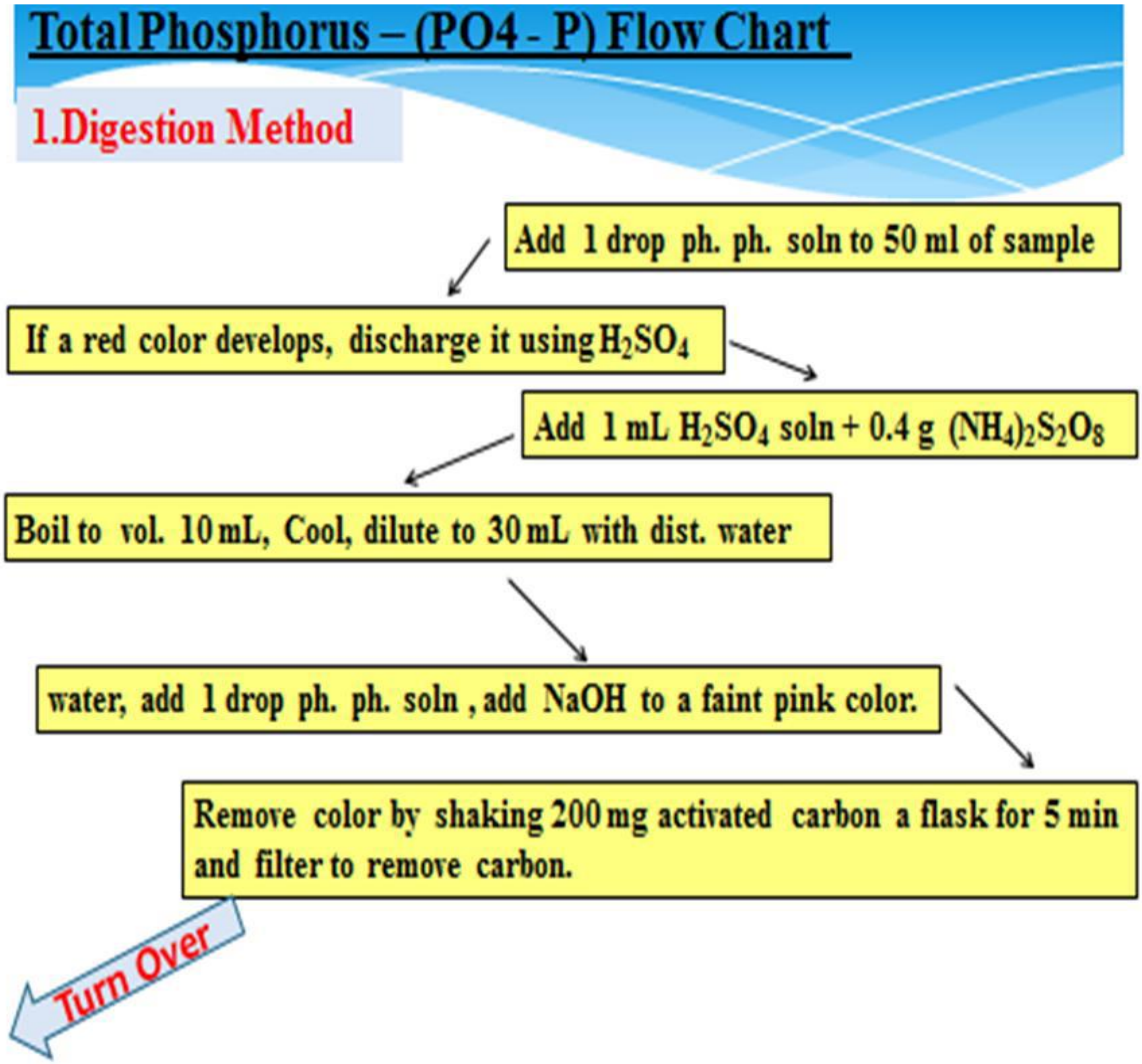
- To aid in method selection, Table 4500-P:I presents the results of various combinations of digestions, hydrolysis, and colorimetric techniques for three synthetic samples of the following compositions:

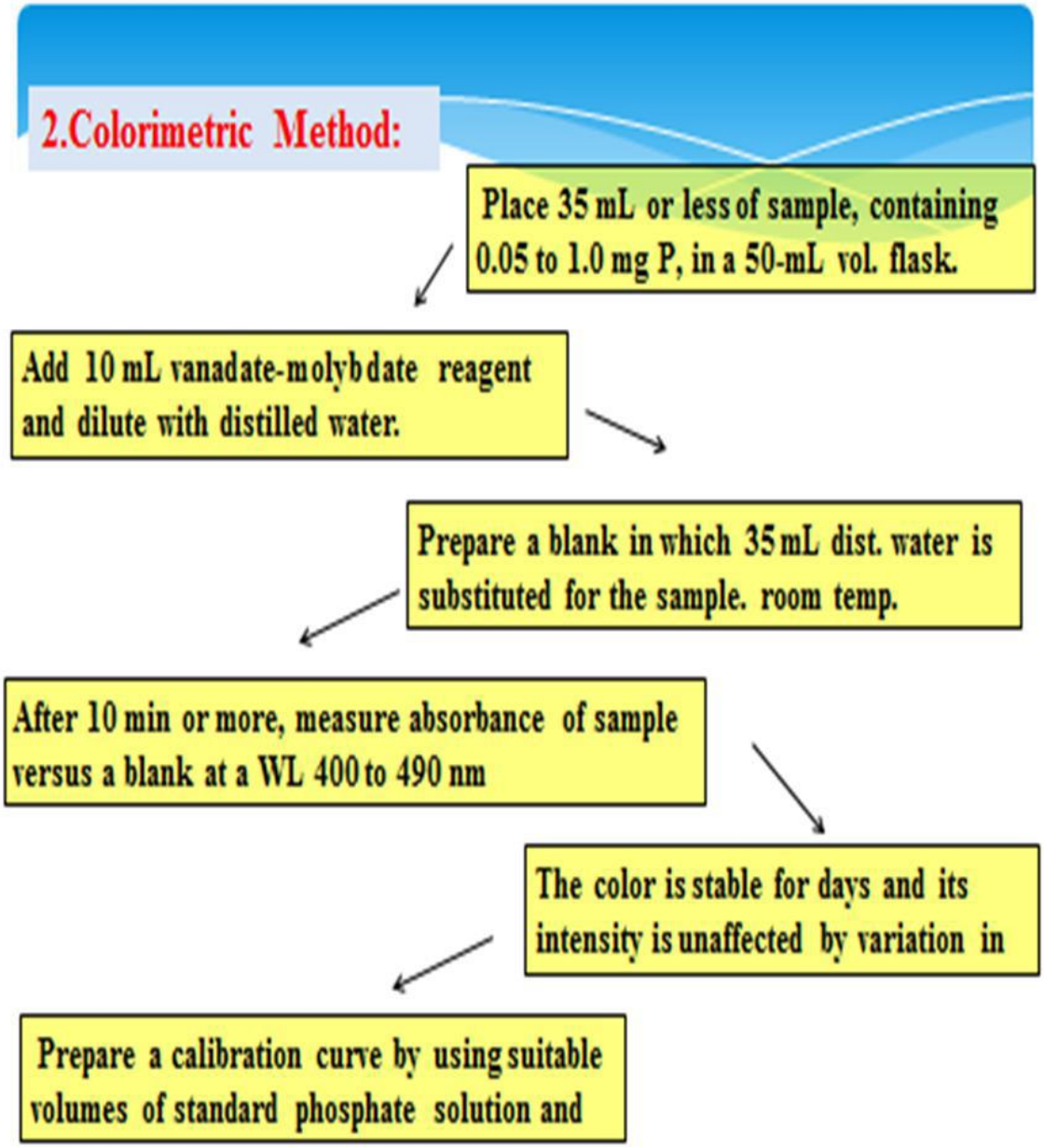
- Sample 1: 100 µg orthophosphate phosphorus PO_4^{3-}-P/L), 80 µg condensed phosphate phosphorus/L (sodium hexametaphosphate), 30 µg organic phosphorus/L (adenylic acid), 1.5 mg NH_3-N/L, 0.5 mg NO_3-N/L, and 400 mg Cl^-/L.
- Sample 2: 600 µg PO_4^{3-}-P/L, 300 µg condensed phosphate phosphorus/L (sodium hexametaphosphate), 90 µg organic phosphorus/L (adenylic acid), 0.8 mg NH_3-N/L, 5.0 mg NO_3-N/L, and 400 mg Cl^-/L.
- Sample 3: 7.00 mg PO_4^{3-}-P/L, 3.00 mg condensed phosphate phosphorus/L (sodium hexametaphosphate), 0.230 mg organic

Reporting Results

NA

Flow chart




2.Colorimetric Method:
Place 35 mL or less of sample, containing 0.05 to 1.0 mg P, in a 50-mL vol. flask.
Add 10 mL vanadate-molybdate reagent and dilute with distilled water.
Prepare a blank in which 35 mL dist. water is substituted for the sample. room temp.
After 10 min or more, measure absorbance of sample versus a blank at a WL 400 to 490 nm
The color is stable for days and its intensity is unaffected by variation in
Prepare a calibration curve by using suitable volumes of standard phosphate solution and

10- Sulphide

Introduction

Method Blank (MB): a sample of laboratory pure water containing no target analyte that is taken through the entire sampling and analytical procedure. In this case, dilution water is used as the blank. The analysis of a method blank helps identifies any contamination introduced in the analysis process.

Duplicate Sample: select routine samples to be analyzed twice. Independently prepare and analyze duplicate samples. Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples. Calculate control limits for duplicates when methods specific limits are not provided.

Laboratory Fortified Blank (LFB): Sample with known concentration of analyte that is used to assess the performance of total analytic system

Principle

This method is taken from Standard Methods for the Examination of water and wastewater edition 23: 4500-S2F. Iodometric Method".

The major portion of the sulfide content in wastewater is produced in the conversion of sulfate (SO_4^{-2}) to sulfide (S^{-2}) by bacteria found in the wastewater.

Oxygen-reducing bacteria will use any available sulfur-containing compound as food.

This process can produce odorous reduced-sulfur compounds including hydrogen sulfide (H_2S), Sulfur-oxidizing bacteria convert the hydrogen sulfide to sulfuric acid which is very corrosive to concrete.

The iodometric method determines total sulfide by titration of sulfide with iodine.

Interference

Reducing substances interfere with this method including thiosulfate, sulfite and various organic compounds. Sample pretreatment may be necessary.

Chemical and reagents

Water: Laboratory distilled water.

6 N Hydrochloric acid

- Transfer by measuring cylinder about 300 ml of distilled water to a 1L beaker.
- add slowly and with stirring 522.8 ml conc. HCl and allow the solution to cool.
- Dilute with distilled water to 1000 ml in a volumetric flask.
- This solution is stable for 3 months, mark with the expiry date.

0.025 N Standard iodine solution

- Dissolve approximately 20 to 25 g potassium iodide in a little distilled water .
- add 3.2 g iodine.
- Transfer the solution to 1L volumetric flask and make up to the mark with distilled water.
- This solution is stable for one month. Mark with the expiry date.

0.025 M Standard sodium thiosulfate titrant

- Dissolve 6.205 g $Na_2S_2O_3.5H_2O$ in distilled water.
- Add 0.4 g solid NaOH and dilute to 1000 ml in a volumetric flask.
- Standardize with bi-iodate solution.
- This solution is stable for one month, Mark with the expiry date.

0.0021 M Standard potassium bi-iodate solution

- Dissolve 812.4 mg $KH(IO_3)_2$ in distilled water and dilute to 1000 ml in a volumetric flask.
- This solution is stable for one month, Mark with the expiry date.

Starch solution

- Dissolve 2 g soluble starch and 0.2 g salicylic acid, as a preservative, in hot distilled water.
- Transfer the solution to a 100 ml volumetric flask and make up to the mark with hot distilled water.
- This solution is stable for 2 months, Mark with the expiry date.

Zinc acetate solution

- Dissolve 220 g $Zn(C_2H_3O_2)$ 2.2 H_2O in 870 ml water, This makes a 1-liter solution.

Quality Control standard

- This standard must not be prepared by the analyst who prepared the other chemicals.
- Dissolve 1.219 g of sodium sulphide in 1000 ml of distilled water.
- This is the 500 mg /L stock sulphide solution.
- This solution must be prepared monthly, mark with the expiry date.
- Pipette 10 ml of the 500 mg/L stock sodium sulphide solution into a 100 ml volumetric flask and dilute to the mark with distilled water.
- This is the 50 mg/L intermediate standard.
- This solution must be prepared daily.
- Pipette 20 ml of the 50 mg/L intermediate standard into a 100 volumetric flask and dilute to the mark with distilled water.
- This is the 10 mg/L quality control solution. This solution must be prepared daily.

Equipment and Supplies

- Balance
- 100, 250, 500, 1000 ml volumetric flasks
- Glass rod
- Volumetric pipettes
- 100 ml conical flasks
- 50, 100 ml cylinders
- Magnetic stirrer & Hot plate
- 25 ml burette
- 100, 400 ml beakers
- Stirrer bars

Sampling

- Collect water samples with minimum aeration. Either analyze samples immediately after collection or preserve with zinc acetate solution for later analysis.
- To preserve a sample for a total sulfide determination, put zinc acetate and sodium hydroxide solutions into sample bottle before filling it with sample.
- Sample bottle before filling it with sample uses 0.2 mL 2M zinc acetate solution per100mLsample.
- Increase volume of zinc acetate solution if the sulfide concentration is expected to be greater than 64 mg/L.
- The final pH should be at least 9.
- Add more NaOH if necessary.
- Fill bottle completely and stopper.
- Sample sediments and sludges under nitrogen atmosphere if possible.
- Store samples at 4°C or frozen, and analyze within 2 weeks (1 month for frozen samples) of collection.
- Do not freeze-dry because acid-volatile sulfide may decompose as a result of oxidation artifacts.

Procedures

Standardization of sodium thiosulfate titrant solution

- Dissolve approximately 2 g KI, free from iodate, in a conical flask with 100 to 150 ml distilled water.
- Add few drops of conc. H_2SO_4 and 20 ml standard bi-iodate solution.
- Dilute to 200 ml and titrate liberated iodine with thiosulfate titrant to a pale straw color.

- Add 2 drops of starch and continue titration till the blue color disappears.
- This is the end point

Standardization of iodine solution

- Transfer into a beaker an amount of iodine, add 2 ml of 6N HCl and dilute to 200 ml.
- Fill a 50 ml burette with standard sodium thiosulfate solution and titrate against the iodine solution.
- adding starch toward end of titration, when a pale straw color is reached.

Sample pre-treatment

- Reducing substances interfere with this method so sample pre-treatment must be done before

Measurement of sample

- Put 0.15 ml zinc acetate solution into a 500 ml glass bottle and fill with a well-shaken sample.
- Add 0.1 ml of 6 N NaOH.
- Stopper with no air bubbles and mix by rotating vigorously about a transverse axis.
- Add further NaOH to bring the pH above 9.
- Let precipitate settle for 30 minutes.
- Sulfide is precipitated out with zinc and zinc sulfide is filtered out, return filters with precipitate to the original bottle and add about 100 ml water.
- Measure the sample within 1 hour.

Sample Determination

- Transfer into a 500 ml beaker an amount of iodine solution estimated to be an excess over the amount of sulfide present.
- Add distilled water, if necessary, to bring volume to about 20 ml and add 2 ml of 6N HCl.
- Pipette 200 ml sample into the beaker, discharging sample under solution surface. If iodine color disappears, add more iodine until color remains.
- Back-titrate with sodium thiosulfate solution, adding a few drops of starch toward end of titration, when a pale straw color is reached.
- Repeat for all samples including the quality control standard and blank

Calculation

$$([\ (A \times B) - (C \times D)\ ] \times 16000)/\text{ml of sample} = \text{mg } S^{-2}/L$$

Where:

A = ml of iodine solution added

B = normality of iodine solution

C = ml of sodium thiosulfate solution added

D = normality of sodium thiosulfate solution

LFB recovery:

$$(Cb/ I) * 100 = \text{Recovery LFB}$$

Where:

Cb = LFB concentration determined experimentally

I = initial concentration from analytes added to LFB.

Relative percent difference:

$$((D1 \_ D2)/((D1 + D2)/ 2))*100 = \%RPD$$

where:

D1 = concentration determined for first duplicate, and

D2 = concentration determined for second duplicate

Quality Control

QC for method	frequency	Acceptance Criteria	Corrective Action:
Method Blank	once per analysis batch	If method blank is <1/2 RL	Re analyze alternative source of blank Check filter paper & filtration system Reanalyze all samples Check calculation. Report in bench sheet " these data are associated writng ablank value that exceeds the detection limits
LFB		LFB recoveries: (according to the validation criteria)	All samples must be reanalyzed If There is not extra sample for reanalysis or holding time expired " the sample must be reported as No result"

Reporting Results

- If the quality control standard result meets the requirements then report the results.
- All results should be reported to the nearest whole number.

11- Biological Oxygen Demand (BOD)

Introduction

The BOD test measures the amount of oxygen used by microorganisms as they use the substrate (food) in wastewater when placed in a controlled temperature, under aerobic conditions.

Principle

BOD analysis does not oxidize all of the organic matter present in the wastewater; only the organics that are biochemically degradable during n days' time period at 20°C are oxidized. The day period is given as index in BODn.

There are two type of organic matter carbonaceous and Nitrogenous organic matter, carbonaceous oxidize at first stage and Nitrogenous organic matter that oxidize after that, so several BOD tested carried out in different purpose.

The standard for usual measurements is a 5-day period at 20°C because at 20°C the bacterial growth is moderate and in dark incubation to prevent photochemical reactions process BOD_5 oxidize 67% of organic matter that almost carbonaceous.

Reaction 1 ($CBOD_5$)

Organics+O_2+ microorganisms $\longrightarrow$ CO_2+H_2O

Reaction 2 (NBOD)

$NH_4^+ + O_2$+microorganisms $\xrightarrow{\text{Nitrosomonus}}$ $NO_2^- + H_2O$

$NO_2^- + O_2$+microorganisms $\xrightarrow{\text{Nitrobacter bacteria}}$ $NO_3^- + H_2O$

In general, a dilution procedure is applied because we can't take 300 ml of sample that contain large amount of organic matter and demand more oxygen.

The test has its widest application in measuring organic loadings to treatment plants and in evaluating the organic matter removal efficiency of such treatment systems. The test measures the molecular oxygen utilized during a specified incubation period for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron.

It also may measure the amount of oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor.

The seeding and dilution procedures provide an estimate of the BOD at pH 6.5 to 7.5.

Many biological treatment plant effluents contain sufficient numbers of nitrifying organisms to cause nitrification in BOD tests. Because oxidation of nitrogenous compounds can occur in such samples, inhibition of nitrification is recommended for samples of secondary effluent, for samples seeded with secondary effluent, and for samples of polluted waters.

The DO (dissolved oxygen) is measured at the beginning and recorded. During the five days period, microorganisms in the sample break down complex organic matter in the sample, using up oxygen in the process.

After the five-day dark incubation period, the DO is again determined. The BOD_5 is then calculated on the basis of the reduction of DO and the size of sample.

This test is an estimate of the availability of food in the sample (food or organisms that take up oxygen) expressed in terms of oxygen use. Results of a BOD_5 test indicate the rate of oxidation and provide an indirect estimate of the availability to organisms or concentration of the waste.

Environmental Conditions:

Actual environmental conditions of temperature, organism population, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained from this test must take into account these factors when relating BOD5 results to receiving water oxygen demands.

Samples for the BOD_5 test should be collected before chlorination because chlorine interferes with the organisms in the test. It is difficult to obtain accurate results with dechlorinated samples.

Samples are incubated for a standard period of five days because a fraction of the total BOD will be exerted during this period. The ultimate or total BOD is normally never run for plant control.

Report results as carbonaceous biochemical oxygen demand ($CBOD_5$) when inhibiting the nitrogenous oxygen demand. When nitrification is not inhibited, report results as BOD5.

Seeding:

Determine BOD of the seeding material as for any other sample. This is the seed control. From the value of the seed control and the knowledge of the seeding material dilution (in the dilution water) determine seed DO uptake. Ideally, make dilutions of seed such that the largest quantity results in at least 50% DO depletion.

A plot of DO depletion, in milligrams per liter, versus ml of seed for all bottles having 2 mg/L depletion and 1.0 mg/L minimum residual DO should present a straight line for which the slope indicates DO depletion per milliliter of seed. The DO-axis intercept is oxygen depletion caused by the dilution water and should be less than 0.1 mg/L. Alternatively, divide DO depletion by volume of seed in milliliters for each seed control bottle having 2 mg/L depletion and 1.0 mg/L residual DO. Average the results for all bottles meeting minimum depletion and residual DO criteria. The DO uptake attributable to the seed added to each bottle should be between 0.6 and 1.0 mg/L, but the number of seed added should be adjusted from this range to that required

providing glucose-glutamic acid check results in the range of 198 ± 30.5 mg/L. To determine DO uptake for a test bottle, subtract DO uptake attributable to the seed from total DO uptake. Adding seeding material to dilution water is described for two sample dilution methods.

Dilution Requirements:

The BOD concentration in most wastewaters exceeds the concentration of dissolved oxygen (DO) available in an air-saturated sample. Therefore, it is necessary to dilute the sample before incubation to bring the oxygen demand and supply into appropriate balance. Because bacterial growth requires nutrients such as nitrogen, phosphorus, and trace metals, these are added to the dilution water, which is buffered to ensure that the pH of the incubated sample remains in a range suitable for bacterial growth. Complete stabilization of a sample may require a period of incubation too long for practical purposes; therefore, 5 d has been accepted as the standard incubation period.

Hazard and Precautions

- The source of dilution water is not restricted and may be distilled, tap or receiving-stream water free of biodegradable organics and bio-inhibitory substances such as chlorine or heavy metals.
- Distilled water may contain ammonia or volatile organics; deionized waters often are contaminated with soluble organics leached from the resin bed.
- Use of copper-lined stills or copper fittings attached to distilled water lines may produce water containing excessive amounts of copper.
- The temperature of the incubator must be at 20 °C. Other temperatures will change the rate of oxygen used.
- The dilution water must be made according to Standard Methods for the most favorable growth rate of the bacteria. This water must be free of copper which is often present when copper stills are used by commercial dealers. Use all glass or stainless-steel stills or demineralized water.
- The wastewater must also be free of toxic wastes, such as hexavalent chromium.
- If you use a cleaning solution to wash BOD bottles, be sure to rinse the bottles several times. Cleaning agents are toxic and if any residue remains in a BOD bottle, the BOD test could be ruined.
- Unchlorinated wastewater normally contains an ample supply of seed bacteria; therefore, seeding is usually not necessary.
- Removal of chlorine carried out by sodium sulphite

Chemical and Reagents

Distilled water

- Water used for solutions and for preparation of the solution water must be of highest quality. It must contain less than 0.1 mg/L copper and be free of chlorine, chloramines, caustic, organic material, and acids

Phosphate buffer solution

- Dissolve 8.5 gm monobasic potassium phosphate (KH_2PO_4), 21.75 gm dibasic potassium phosphate (K_2HPO_4), 33.4 gm dibasic sodium phosphate crystals ($Na_2HPO_4.7H_2O$), and 1.7 gm ammonium chloride (NH_4CI) in distilled water and make up to 1 liter.
- The pH of this buffer should be 7.3 and should be checked with a pH meter.
- Discard this reagent if there is any sign of biological growth.

Magnesium sulfate solution

- Dissolve 22.5 gm magnesium sulfate crystals ($MgSO_4.7\ H_2O$) in distilled water and make up to 1 liter.

Calcium chloride solution

- Dissolve 27.5 gm anhydrous calcium chloride ($CaCI_2$) in distilled water and make up to 1 liter.

Ferric chloride solution

- Dissolve 0.25 gm ferric chloride ($FeCI_3.6H_2O$) in distilled water and make up to 1 liter.

Dilution water

- Add 1 ml each of phosphate buffer, magnesium sulfate soln , calcium chloride soln, and ferric chloride solutions for each liter of distilled water.
- Saturate with DO by shaking in a partially filled bottle or by aerating with filtered air.
- Store at a temperature as close to 20 °C as possible for at least 24 hours to allow the water to become stabilized.
- This water should not show a drop in DO of more than 0.2 mg/l on incubation for five days.

For unchlorinated samples

- The test is made by measuring the oxygen used or depleted during a five days period at 20 °C by a measured quantity of wastewater sample seeded into a reservoir of dilution water saturated with oxygen.
- This is compared to an unseeded or blank reservoir of dilution water by subtracting the difference and multiplying by a factor for dilution.

Equipment and Supplies

- 300 ml BOD bottles with ground glass stoppers
- Incubator, 20 °C ± 1 °C
- Pipets, 10 ml graduated, (0.8- to 1.6-mm) diameter tip
- Burette and stand
- Erlenmeyer flask, 500 ml
- DO. meter.

Procedures

- BOD bottles should be of 300 ml capacity with graduations and ground-glass stoppers.
- To clean the bottles, carefully rinse with tap water followed by distilled water.
- Fill two bottles completely with dilution water and insert the stopper tightly so that no air is trapped beneath the stopper.
- Siphon dilution water from its container when filling BOD bottles.
- Set up one or more dilutions of the sample to cover the estimated range of BOD values. From the estimated BOD.
- Calculate the volume of raw sample to be added to the BOD bottle based on the fact that:
- The most valid DO depletion is 4 mg/L.
- Therefore, ml of sample added per 300 ml

$$= \frac{(4mg\ /\ 1)\ X\ (300ml)}{Estimated\ BOD,mg/L} = \frac{1200}{Estimated\ BOD,mg/L}$$

- **For Example:** If Estimated BOD = 400 mg/l , then the ml of sample added per 300 ml $= \frac{1200}{400} = 4$ ml , And when Estimated BOD = 200 mg/l: use 6 ml , by the same when 100 mg/l: use12 ml, And when 20 mg/l: use 60 ml.
- When the BOD is unknown, select more than one sample size, for example, place several samples 1 ml, 3 ml, 6 ml, and 12 ml-into four BOD bottles. For samples with very high BOD values, it may be difficult to accurately measure small volumes or to get a truly representative sample. In such a case, initial dilution should first be made on the sample. A dilution of 1:10 is convenient.
- To perform the BOD test, first fill two BOD bottles with BOD dilution water (blanks). Nos. (1) and (2).
- Next, for each sample to be tested, carefully measure out the two portions of sample and place them into two new BOD bottles, Nos. (3) and (4). Add dilution water until

the bottles are completely filled. Insert the stoppers. Avoid entrapping air bubbles. Be sure that there are water seals on the stoppers.

- On bottles (2) and (4) immediately determine the initial dissolved oxygen.
- Incubate the remaining dilution water blank and diluted sample in the dark at 20 °C for five days. These are bottles (1) and (3).
- At the end of exactly five days (±3 hours), test bottles (1) and (3) for their Dissolved Oxygen by using the DO probe. At the end of five days, the oxygen content should be at least 1 mg/L. Also, a depletion of 2 mg/L or more is desirable. Bottles (1) and (2) (blanks) are only used to check the dilution water quality. Their difference should be less than 0.2 mg/L after five days if the quality is good and free of impurities. The difference in blank readings is not used as a blank correction, but merely as a check on the quality of dilution water. Differences of greater than 0.2 mg/l could possibly be due to contamination and /or dirty BOD bottles.

Calculation

$$\mathbf{BOD_5\ mg/L} = \frac{(A-B)\ X\ V}{Sample\ Volume}$$

Where:

(A) is Initial DO of Diluted Sample

(B) is DO of Sample and Dilution after 5 days Incubation

(V) is the sample bottle volume= 300ml

Reporting Results

NA

12- Chemical Oxygen Demand (COD)

Introduction

Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions.

Principle

The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. Because of its unique chemical properties, the dichromate ion ($Cr_2O_7^{2-}$) is the specified oxidant in Methods of the Standard Methods 20th edition; it is reduced to the chromic ion (Cr^{3+}) in these tests. Both organic and inorganic components of a sample are subject to oxidation, but in most cases the organic component predominates and is of the greater interest. COD is a defined test; the extent of sample oxidation can be affected by digestion time, reagent strength, and sample COD concentration.

COD often is used as a measurement of pollutants in wastewater and natural waters.

Other related analytical values are biochemical oxygen demand (BOD_5), total organic carbon (TOC), and total oxygen demand (TOD).

In many cases it is possible to correlate two or more of these values for a given sample.

- ❖ BOD is a measure of oxygen consumed by microorganisms under specific conditions.
- ❖ TOC is a measure of organic carbon in a sample.
- ❖ TOD is a measure of the amount of oxygen consumed by all elements in a sample when complete (total) oxidation is achieved.

In a COD analysis, hazardous wastes of mercury, hexavalent chromium, sulfuric acid, silver, and acids are generated. Closed reflux method reduces these waste problems.

Closed Reflux, Colorimetric Method

- When a sample is digested, the dichromate ion oxidizes oxidizable material in the sample.
- This results in the change of chromium from the hexavalent (VI) state to the trivalent (III) state.
- Both of these chromium species are colored and absorb in the visible region of the spectrum.
- The dichromate ion ($Cr_2O_7^{2-}$) absorbs strongly in the 400 nm region, where the chromic ion (Cr^{3+}) absorption is much less.
- The chromic ion absorbs strongly in the 600 nm region, where the dichromate has nearly zero absorption.

- In 9M sulfuric acid solution, the approximate molar extinction coefficients for these chromium species are as follows: Cr^{3+}- 50 L/mole cm at 604 nm; $Cr_2O_7^{2-}$- 380 L/mole cm at 444 nm; Cr^{3+}- 25 L/mole cm at 426 nm. The Cr3+ ion has a minimum in the region of 400 nm. Thus, a working absorption maximum is at 420 nm.
- For COD values between 100 and 900 mg/L, increase in Cr^{3+} in the 600 nm region is determined. Higher values can be obtained by sample dilution. COD values of 90 mg/L or less can be determined by following the decrease in $Cr_2O_7^{2-}$ at 420 nm.
- The corresponding generation of Cr^{3+} gives a small absorption increase at 420 nm, but this is compensated for in the calibration procedure.

Interference

- Straight-chain aliphatic compounds are oxidized more effectively in the presence of a silver sulfate catalyst,
- the most common interferent is the chloride ion.
- Chloride reacts with silver ion to precipitate silver chloride, and thus inhibits the catalytic activity of silver.
- Bromide, iodide, and any other reagent that inactivates the silver ion can interfere similarly. Results then are in error on the high side.
- The difficulties caused by the presence of the chloride can be overcome largely, though not completely, by complexing with mercuric sulfate ($HgSO_4$) before the refluxing procedure. Although 1 g $HgSO_4$ is specified for 50 mL sample, a lesser amount may be used where sample chloride concentration is known to be less than 2000 mg/L, as a 10:1 weight ratio of $HgSO_4$: Cl^- is maintained.
- Do not use the test for samples containing more than 2000 mg Cl–/L. Techniques designed to measure COD in saline waters are available.1,2 Halide interferences may be removed by precipitation with silver ion and filtration before digestion.
- This approach may introduce substantial errors due to the occlusion and carry down of COD matter from heterogenous samples.
- Ammonia and its derivatives, in the waste or generated from nitrogen-containing organic matter, are not oxidized. However, elemental chlorine reacts with these compounds. Hence, corrections for chloride interferences are difficult.
- Nitrite (NO_2^-) exerts a COD of 1.1 mg O_2/mg NO_2-N. Because concentrations of NO_2– in waters rarely exceed 1 or 2 mg NO_2-N/L, the interference is considered insignificant and usually is ignored.

- To eliminate a significant interference due to NO_2^-, add 10 mg sulfamic acid for each mg NO_2-N present in the sample volume used; add the same amount of sulfamic acid to the reflux vessel containing the distilled water blank.
- Reduced inorganic species such as ferrous iron, sulfide, manganous manganese, etc., are oxidized quantitatively under the test conditions.
- For samples containing significant levels of these species, stoichiometric oxidation can be assumed from known initial concentration of the interfering species and corrections can be made to the COD value obtained.
- The silver, hexavalent chromium, and mercury salts used in the COD determinations create hazardous wastes.
- The greatest problem is in the use of mercury. If the chloride contribution to COD is negligible, $HgSO_4$ can be omitted. Smaller sample sizes.

Hazard and Precautions

- Sample volume used according to the spectrophotometer method is 2 ml.
- Preferably analyze samples in duplicate because of small size used.
- Samples that are inhomogeneous may require multiple determinations for accurate analysis.
- These should not differ from their average by more than: 1.5% for the high-level COD test unless the condition of the sample dictates otherwise.

Chemical and Reagents

Digestion solution, high range

- Add to about 500 mL distilled water 10.216 g $K_2Cr_2O_7$, primary standard grade, previously dried at 150°C for 2 h, 167 mL conc H_2SO_4, and 33.3 g $HgSO_4$. Dissolve, cool to room temperature, and dilute to 1000 mL.

Digestion solution, low range

- Prepare as in above, but use only 1.022 g potassium dichromate.

Sulfuric acid reagent

- Add Ag_2SO_4, reagent or technical grade, crystals or powder, to conc H_2SO_4 at the rate of 5.5 g Ag_2SO_4/kg H_2SO_4. Let stand 1 to 2 d to dissolve.

Sulfamic acid

- Required only if the interference of nitrites is to be eliminated

Potassium hydrogen phthalate standard

- Lightly crush and then dry KHP to constant weight at 110°C.

- Dissolve 425 mg in distilled water and dilute to 1000 ml. KHP has a theoretical COD1 of 1.176 mg O_2/mg and this solution has a theoretical COD of 500 µg O_2/ mL
- This solution is stable when refrigerated, but not indefinitely.
- Be alert to development of visible biological growth. If practical, prepare and transfer solution under sterile conditions.
- Weekly preparation usually is satisfactory.

Equipment and Supplies

- Digestion vessels: Preferably use borosilicate culture tubes, 16- × 100-mm, 20- × 150-mm, or 25- × 150-mm, with TFE-lined screw caps. Alternatively, use borosilicate ampules,10-mL capacity, 19- to 20-mm diam. Digestion vessels with premixed reagents and other accessories are available from commercial suppliers.
- Block heater or similar device to operate at 150 ± 2°C, with holes to accommodate digestion vessels. Use of culture tubes probably requires the caps to be outside the vessel to protect caps from heat. CAUTION: Do not use an oven because of the possibility of leaking
- samples generating a corrosive and possibly explosive atmosphere. Also, culture tube caps may not withstand the 150°C temperature in an oven.
- Micropipette.
- Spectrophotometer, for use at 600 nm and/or 420 nm with access opening adapter for ampule or 16-, 20-, or 25-mm tubes. Verify that the instrument operates in the region of 420 nm and 600 nm. Values slightly different from these may be found, depending on the spectral bandpass of the instrument.

Procedures

- **Treatment of samples**: Measure 2 ml of sample (or a diluted sample) into a digestion tube indicated in the manufacturer instructions. Prepare, digest, and cool samples, blank, and one or more standards. It is critical that the dilution factor of each sample be known and that the total volume is the same for each reaction vessel (2 ml).
- **Measurement of dichromate reduction**: Cool sample to room temperature slowly to avoid precipitate formation. Once samples are cooled, vent, if necessary, to relieve any pressure generated during digestion. Mix contents of reaction vessels to combine condensed water and dislodge insoluble matter. Let suspended matter settle and ensure that optical path is clear. Measure absorption of each sample blank and standard at selected wavelength (420 nm or 600 nm). Analyze a digested blank to confirm good analytical reagents and to determine the blank (to set the zero value).

- Preferably analyze samples in duplicate because of small sample size. Samples that are inhomogeneous may require multiple determinations for accurate analysis.

Calculation

If sample, standard, and blanks are run under same conditions of volume and optical path length, calculate COD as follows:

$$\text{COD as } O_2 \text{ / L} = \frac{mg\ O2\ in\ final\ volume\ \ X\ 1000}{ml\ sample}$$

Reporting Results

NA

13- Oil & Grease

Introduction

Oil and grease are defined as any material recovered as a substance soluble in the solvent (petroleum ether), it includes other material extracted by the solvent from an acidified sample. Oil and grease are measured in raw waste water & out let waste water.

Increase in Oil and grease value in raw waste water refers to presence of industrial waste water. It is harmful for biological treatment as it prevents oxygen to dissolve in waste water so bacteria are died.

Principle

Oil and grease are an organic compound which extracted by addition an organic solvent in acidic medium, can be measured by gravimetric method.

Interference

Organic solvents have the ability to dissolve not only oil and grease but also other organic substances, any filterable solvent soluble substances (e.g., elemental sulfur, complex aromatic compounds, hydrocarbon derivatives of chlorine, sulfur, and nitrogen, and certain organic dyes) that are extracted and recovered.

Chemical and Reagents

a. Hydrochloric or sulfuric acid, 1:1: Mix equal volumes of either acid and reagent water.

b. n-Hexane, 85% minimum purity, 99% minimum saturated C6 isomers, residue less than 1 mg/L; distill if necessary.

Equipment and Supplies

- Separating funnel
- Water bath
- Drying oven
- Dissector
- Electronic balance

Sampling

- Collect a representative grab sample in a wide- mouth glass bottle that has been washed with soap, rinsed with water, and finally rinsed with solvent to remove any residues that might interfere with the analysis.
- Do not overfill the sample container and do not subdivide the sample in the laboratory.
- If analysis is to be delayed for more than 2 h, acidify to pH 2 or lower with either 1: 1HCl or 1: 1 H_2SO_4 and refrigerate

Procedures

- collect 500 ml sample in aclean 1000 ml seperatory finnel.
- Add 4 ml of 1:1 HCL, mix well, pH must be 2.
- Weigh dried and record the weight of flask. (A)
- Add 20 ml of n-Hexane to the sample.
- shake well, wait few minutes until oil &grease float.
- Separate oil &grease layer in weighed flask
- put flask with oil on water bath then drying by oven.
- cool in dissector.
- weigh flask with oil after drying. (B)

Calculation

$$\text{mg oil and grease/l} = \frac{(A-B)\times 1000\times 1000}{\text{ml sample}}$$

Quality Control

Section	Method Blank	LFB	LFM
5520 B	X	X	X

- Duplicates of the sample**:** %RPD within +_10%

Reporting Results

NA

قام بإعداد الإصدار الثانى من هذا البرنامج

د/ حسام الشربيني	شركة الإسكندرية للصرف الصحي
د/ حازم حسن رجب	شركة القاهرة للصرف الصحي
د/ عماد جمعة عبد الفتاح	شركة المنوفية لمياه الشرب والصرف الصحي
كيميائي/محمد ماهر محمد	المعمل المرجعي للصرف الصحي- الشركة القابضة
كيميائية/ مروة رضا جمعة	شركة دمياط لمياه الشرب والصرف الصحي
كيميائية/ ميادة دياب بنداري	شركة الشرقية لمياه الشرب والصرف الصحي

قام بالتنسيق الفنى والإخراج لهذا الإصدار

كيميائي/ محمد الصوفي زين العابدين	المعمل المرجعي للصرف الصحي- الشركة القابضة
كيميائي/ محمود جمعه	الإدارة العامة للمسار الوظيفى- الشركة القابضة

حقوق الطبع محفوظة
الإدارة العامة للمسار الوظيفى - إدارة المناهج
الشركة القابضة لمياه الشرب والصرف الصحي

للاقتراحات والشكاوى قم بمسح الصورة (QR)