

WATER AND WASTE WATER TECHNOLOGIES

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1. WATER ANALYSES

1.1. PURPOSE OF WATER ANALYSIS

Water is not a matter only used industry but also we use in every part of our life for different purposes. In every unit of the chemical industry there is a need for water as process water or for other purposes. Boiler bseleme, cooling, washing, dissolving, humidifying processes such as water is the auxiliary. Water is a raw material in the production of beer and soft drinks and in the process of quenching lime.

The use of water outside the industry is also very wide. In order to produce irrigation water, drinking water, laundry water and fish, a large amount of fresh water is needed.

Surface and groundwater in nature are usually fresh water. These waters contain less than 1 g / l of dissolved salt. These salts are transferred to the water through the environments they pass through. As a result, it is necessary to determine whether the type and amount of salts dissolved in surface and groundwater are suitable for their intended use. If not applicable, the harmful components contained in the product must be removed.

Fresh water is required to comply with certain characteristics such as drinking water, agricultural irrigation water, boiler feed water or industrial water. These properties are determined by chemical analysis.

On the other hand, water is contaminated when used. Polluted waters are not used and they pollute the receiving environment such as creek, lake and sea where these waters have been thrown, and they have harmful effects on the environment. Therefore, it is necessary to analyze the polluted water to determine what is contaminated. Dirty waters can be grouped into three main groups. Domestic wastewater, industrial wastewater, rainwater from city streets and squares. Experiments on composite samples taken periodically to determine the degree of pollution of water are required. Which analysis shall be carried out in clean water shall be determined by taking into consideration the usage area of the water. The analyzes to be carried out in polluted waters are also determined by taking into account the type of contamination and the parameters given by the Ministry of Environment Dirty Water Regulation. In this regulation, the discharge conditions and pollution limit values of the wastewater of each industry are given to the environment.

Below are the main experiments that should be done in drinking water and household wastewater.

Analysis of drinking water:

1. pH
2. Electrical conductivity
3. Blur
4. alkalinity
5. Hardness
6. Chloride
7. Total Dissolved Salts
8. Ammonia
9. Nitrite
10. Organic Substance

Analysis of domestic wastewater:

1. Suspended Total Solids
2. Collapsible Substances
3. Dissolved Oxygen

4. Chemical Oxygen Demand
5. Biochemical Oxygen Demand
6. Ammonia nitrogen
7. Nitrite nitrogen
8. Phosphate
9. Oil
10. detergent

In the water, it may be necessary to analyze heavy metals such as Pb + 2, Hg + 2, Cd + 2, Zn + 2, Cr + 3, Fe + 2 and organic pollutants such as phenol, aniline and agricultural preservatives.

Some of the important analysis methods are given here.

1.2. pH DETERMINATION

The negative logarithm of H^+ ions in water is defined as pH. In pure water, $H = 10^{-7}$, $pH = 7$. Dissolved carbon dioxide in the natural water is converted into carbonic acid, causing pH to decrease. Alkali salts form OH-ions as hydrolysis and increase the pH value of water.

The pH of the waters is most easily measured by the pH meter device. This device is basically a voltmeter and is based on measuring the potential of the hydrogen electrode by means of a reference electrode.

Calibration of pH meter:

Before the pH meter is used, the pH value should be calibrated with the buffer solutions which are certain and constant. The most commonly used buffer solution is $pH = 7$. If this solution is not available, $pH = 7$ buffer solution can be prepared in the laboratory.

$pH = 7$ buffer solution 1.361 g of anhydrous potassium hydrogen phosphate (KH_2PO_4) and 1.420 g of disodium hydrogen phosphate (Na_2HPO_4) are dissolved in a small amount of water and complete with one liter of distilled water. The pH of this buffer solution is 7.0.

1.2.1. Experimental Procedure

The pH meter is expected to warm up for 15 minutes. The temperature of the sample water is measured, the temperature setting knob on the device is set to the measured temperature to measure the pH value at 25 °C. With the $pH = 7.0$ buffer solution, measurement of the device is done

by measuring. The electrodes are removed, washed with distilled water, dried with filter paper. The pH of the sample water is read from the instrument's indicator.

1.3. Electrical Conductivity Determination

The electrical conductivity unit is Siemens. 1 siemens (S) = 1 / Ohm = 1 Ohm⁻¹ = 1mho. Based on this definition, the resistance of the water as Ohm.cm is measured. In contrast, the conductivity of Ohm⁻¹.cm⁻¹ is calculated.

The resistance is calculated with the following correlation.

$$R = \rho \frac{l}{A}$$

Here R: Resistance, Ohm

ρ = Self resistance, Ohm.cm

l = Length, cm

A = The cross-sectional area is cm².

Self conductivity κ (Capa)

$$\kappa = \frac{l}{RA}$$

if the value is replaced,

$$R = \frac{l}{\kappa A}$$

obtained. For devices used in conductivity measurements, l / A = K is fixed. It's called cell constant. If this value is replaced, the conductivity

$\kappa = \frac{K}{R}$ ohm⁻¹.cm⁻¹. Since (K) is constant, the inverse of the measured resistance value gives the conductivity.

Naturally, the conductivity in the waters is very small. For this reason, the shaft or micro values are usually given. The higher the concentration of dissolved salts in water, the greater the conductivity value.

1.3.1. Experimental Procedure

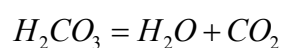
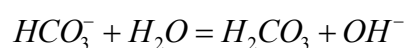
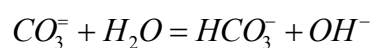
In the assay, a cell constant is known. The value read is multiplied by this cell constant. A 0.01 M potassium chloride solution is used to calibrate the instrument. The conductivity of this solution at 25 °C is 0.00141 ohm⁻¹.cm⁻¹.

The conductivity varies according to the temperature of the water. The temperature in the reports is 25 °C. For this reason, the measured values of t °C are measured. Temperature factors are given below.

Temperature ⁰ C	Factor f
15	1.247
16	1.216
17	1.189
18	1.163
19	1.136
20	1.112
21	1.087
22	1.064
23	1.043
24	1.020
25	1.000

1.4. ALKALINE DETERMINATION

Since the carbonate and bicarbonate ions in the natural waters are weak acid salts, they increase the pH of the water in the basic direction as a result of the hydrolysis. Carbon dioxide and carbonate ions dissolved in water are in equilibrium.



The acid constant for the first hydrogen of the carboxylic acid is the acid constant $k = 4.7 \times 10^{-11}$ for the second hydrogen of $k = 4.3 \times 10^{-7}$. Therefore, carbonate ion is more basic than bicarbonate ion. In the case of carbonate ion in water, pH > 9 will be. The phenol ftalein indicator at this pH is purple. If no carbonate ion is present in the water, the phenol ftalein indicator remains colorless. Similarly, the bicarbonate anion in water stain the color of the methyl ratio to yellow.

Alkalinity assays are performed using these indicators. The alkalinity resulting from the carbonate ion is called the phenol Ftalein alkalinity in (P). The leading alkalinity of bicarbonate is called the Or Methyl alkalinity of Methyl in (M). The sum of these two is called the total alkalinity (T).

1.4.1. Required Solutions

1. Phenolftalein indicator solution:

5g phenolphthalein 500 ml dissolved in 95% alcohol. Add 500 ml of distilled water. The mixture is titrated with 0.02 N NaOH solution until a light pink color occurs. The turning point of this indicator is pH = 8.2-8.3.

2. Methyl Oranj indicator solution:

Dissolve 0.5 g of methyl in distilled water at 1000 ml. The turning point of this indicator is pH = 4-5.

3. Standard 0.02 N H₂SO₄ solution:

0.563 ml of H₂SO₄ (d = 1.84) is taken from 96% and distilled to 1000 ml with distilled water. This solution is adjusted to a solution of 0.02 N Na₂CO₃. 1ml of this solution is equivalent to 1 mg CaCO₃.

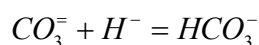
4. 0.02 N Sodium Carbonate Solution

At 140 °C, weighed 1.060 g of dried Na₂CO₃ in the oven and completed with 1000 ml of carbon dioxide-free distilled water.

1.4.2. Experimental Procedure

50 ml of water is taken. A drop of 3-5 drops of phenol ftalein solution is dropped. If there is no purple color in the solution, there is no carbonate ion in the water. In this case the phenolphthalein alkalinity of water is understood to be zero.

When the phenolphthalein indicator is dripped, if the purple color is formed, the carbonate ion is titrated with 0.02 N H₂SO₄ until the indicator color disappears. The following reaction occurs in water.



That is, the carbonate ion is converted into an equivalent amount of bicarbonate ion. Thus, the purple color of the phenolphthalein is lost. The amount of acid spent in the titration of the carbonate ion (P) is recorded by reading the ml.

The same sample is also used for the determination of bicarbonate ion. For this, on the sample this time, 3-5 drops of methyl content indicator is dropped. The solution gets a yellow color. The color is titrated with 0.02 N H₂SO₄ until it changes to orange color. The amount of acid used is recorded by reading (M) ml.

1.4.3. Calculation

Phenol is calculated in CaCO₃ with the following correlation of the ftalein alkalinity.

$$\text{Phenolftalein alkalinity} = P \times N \times \frac{50000}{V}$$

Here, P = acid spent in titration, ml

N = Normality of Acid, (0.02)

V = Sample volume is ml.

For example, if P = 1 ml of acid is spent in the titration with phenolphthalein 50 ml, for example, the carbonate ion is titrated up to bicarbonate.

$$\text{Phenol ftalein alkalinity} = 2 \times 1 \times 0.02 \times \frac{50000}{V}$$

$$\text{Phenol ftalein alkalinity} = 40 \text{ ppm CaCO}_3$$

The methyl content alkalinity is calculated in calcium carbonate with the following correlation.

$$\text{Methyl Oranj Alkalinity} = \frac{M \times N \times 50000}{V}$$

Here M = acid spent in titration, ml

N = normality of the acid, (0.02 N)

V = Sample volume is ml.

For example, after spending for P = 1 ml phenolphthalein, M = 5 ml of methyl content of the actual acid consumption M = 5-1 = 4 ml.

$$\text{Alkaline Alkaline Methyl} = \frac{4 \times 0.02 \times 5000}{50}$$

Methyl alcohol content = 80 ppm CaCO_3

If P = 0, the amount of direct M is used in the calculation.

NOTE:

Although not found in natural waters, wastewater or wastewater in chemical processes may have some OH^- ion present. This ion is titrated with the CO_3^{2-} ion in the same experiment with the phenolphthalein indicator. When the CO_3^{2-} ions are titrated HCO_3^- formed, However when the OH^- ion is titrated water is formed. Considering this situation, it is possible to calculate the values of hydroxide carbonate and bicarbonate alkalinity separately at the end of titration.

The alkalinity of phenolphthalein alkalinity (P) ml, the amount of acid used for the methyl content alkalinity (M) ml and the total acid expenditure (P + M) = T ml, the alkalinity values can be calculated differently for the following 5 states.

Titration results	Alcalinitiy type		
	Hydroxide	Carbonate	Bicarbonate
First state P=0	0	0	T
Second state P< T/2	0	2P	T-2P
Third state P=T/2	0	2P	0
Fourth state P> T/2	2P-T	2(T-P)	0
Fift state P=T	T	0	0

This table obtained according to the results of titration is interpreted as follows.

- First state: (P = 0)

There is no hydroxide and carbonate alkalinity in water. All acid consumption was spent for bicarbonate.

-Second State: ($P < T / 2$)

There is no hydroxide ion in water. The amount of P spent on the phenolphthalein indicator was spent to convert the carbonate to bicarbonate. Therefore, carbonate alkalinity should be 2P. The actual consumption for bicarbonate will be $T - 2P$.

-Third state: ($P = T / 2$)

In this case, there is no hydroxide ion in water. The amount of acid spent for the phenolphthalein indicator was spent on carbonate. Since $2P = T$, there is no bicarbonate ion in water.

Fourth State: ($P > T / 2$)

There are hydroxide and carbonate ions in water. Acid consumption ($2P - T$) spent for the hydroxides ion. For carbonate, 2 (T-P) ml were spent on acid. There is no bicarbonate ion in water.

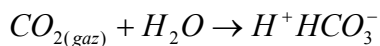
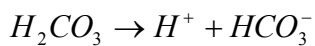
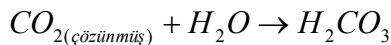
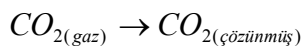
Fifth state: (P-T)

This state occurs only in the presence of hydroxide ions in water.

In natural waters, there may be first and second cases.

1.5. DETERMINATION OF FREE CARBON DIOXIDE

In natural surface waters, dissolved carbon dioxide is less than 10 mg / l. However, some groundwater can have very high levels of carbon dioxide. Carbon dioxide, dissolved in water, is in equilibrium with the bicarbonate ion in the water.



This depends on the equilibrium temperature and the gas pressure that interacts with water. Therefore, in order to obtain the actual value, the free carbon dioxide test must be carried out as soon as the sample is taken.

1.5.1. Solutions Required

1- 0.0454 N Sodium Carbonate Solution:

Weigh 2.407 g of anhydrous sodium carbonate dried in 140 °C. The CO₂-free distilled water which has been boiled and cooled to room temperature is dissolved in water and completed to 1 liter. 1 ml = 1 mg CO₂ in this solution.

2- Phenolphthalein indicator solution:

5 g of phenolphthalein disodium salt is dissolved in distilled water to 100 ml.

1.5.2. Experimental Procedure

Take 100 ml of water sample into a 100 ml flask (metered cylinder). When the sample is taken, it is appropriate to flush it into the dissolved carbon dioxide so that it does not escape. The container is filled with water until it is transported. Then the upper part of the water is poured into 100 ml is set.

Add 3-5 drops of phenolphthalein to the sample. If pink color occurs, it is understood that there is no free carbon dioxide in the water. If the sample does not produce color with the phenolphthalein indicator, the amount of free carbon dioxide is titrated with sodium carbonate solution. Titration should be continued for at least 30 seconds until a permanent pink color occurs.

1.5.3. Calculation

The amount of free carbon dioxide in the water is calculated by the following correlation.

$$\text{Carbon dioxide} = \frac{S \times N \times 22000}{V} \text{ mg / l}$$

Here, S = volume of spent sodium carbonate for titration, ml

N = Normality of sodium carbonate solution

V = Sample volume, ml

For example: 2 ml of 0.0454 N sodium carbonate for 100 ml sample

$$\text{Karbodioksit} = \frac{2 \times 0.0454 \times 22000}{100} = 20 \text{ mg / l}$$

The amount of free carbon dioxide in the water can also be found graphically using specific nomograms prepared for this purpose.

As explained above, the free carbon dioxide in water depends on the pH range and the HCO_3 concentration of water. Considering the above equilibrium reaction, as the pH of the waters increases (as the H^+ ion decreases) and the bicarbonate alkalinity decreases, the amount of free carbon dioxide will decrease.

1.6. HARDNESS DETERMINATION

The sum of divalent metal ions such as Ca^{2+} , Mg^{+2} in water is called hardness. Hardness can be expressed in various units. The most commonly used hardness units are as follows.

1 French hardness = 10 mg CaCO_3 / liter

1 German hardness = 10 mg CaO / liter

1 ppm hardness = 10 mg CaCO_3 / liter

1 milliequivalent hardness = 50 mg CaCO_3 / liter

The hardness ions in water are expressed in terms of calcium carbonate, regardless of hardness.

Considering the water's alkalinity value, it is possible to divide the hardness of the water into "temporary hardness" and "permanent hardness". If calcium and magnesium are present in water with a bicarbonate ion attached to it, this is called temporary hardness (or carbonate hardness). If calcium and magnesium are in water together with ions such as chloride and sulfate, this is called permanent hardness. Such distinction is caused by the temporary hardness being precipitated by the following reaction if the water is heated.



This reaction is caused by the fact that water with temporary hardness makes a boiler scale.

Temporary hardness and permanent hardness sum are called total hardness. Generally the total hardness is determined in water.

Temporary and permanent hardness values are calculated by considering the total hardness and alkalinity values determined experimentally. These accounts are made according to the following principles. The values of total hardness and methyl content alkalinity can be one of the following two states.

First state:

Methyl orange alkalinity $\gg$ Total hardness

In this case, all of the hardness in water is in temporary hardness. Permanent hardness is zero.

Second state:

Methyl orange alkalinity $<$ total hardness

In this case, the temporary hardness = methylorange alkaline will be. Permanent hardness is found with the following relation.

Permanent hardness = total hardness – Methyl orange alkalinity

Determination of Total Hardness:

Ca^{++} , Mg^{++} ions dissolved in water are bound by complexing with iyon ethylene diamine tetra acetic acid iyon EDTA compound. Ca^{+2} and Mg^{+2} ions can be titrated with 0.01 N EDTA solution using a special indicator.

1.6.1. Solutions to be used

1- 0.01 N EDTA (Ethylene Diamine Tetra Acetic Acid Sodium Salt) solution:

1.86 g EDTA is dissolved in distilled water and made up to 1000 ml. This solution is adjusted against the standard calcium chloride solution.

2- 0.01 N Standard Calcium Chloride Solution:

Weigh 0.5 g of pure calcium. Add 3 ml of a 1 to 9 dilute hydrochloric acid solution to dissolve the calcium carbonate in the acid and convert to calcium chloride. Then add to 1000 ml with distilled water. This solution is equivalent to 1 ml = 0.5 mg calcium carbonate. This solution is used to adjust the EDTA solution.

3- Eriochrome Black-T Indicator (solid)

0.5 g of Eriochrome black-T indicator and 100 g of sodium chloride are crushed in a mortar and mixed thoroughly. This indicator can be used for a long time.

4-Buffer Solution:

1.179 g of EDTA disodium salt and 780 mg of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ are dissolved in 50 ml of distilled water. 16.9 g of NH_4Cl and 143 ml of concentrated ammonia are added to this solution and diluted with distilled water to 250 ml.

1.6.2. Experiment procedure

50 ml of water is taken. Put 1 ml of buffer solution and a spatula tip in place of the solid eriochrome black T indicator. The solution gets a red color. With 0.01 N EDTA solution, the color is titrated from red to blue.

1.6.3. Calculation

Total hardness is calculated with the following correlation in ppm CaCO_3 .

$$\text{Total Hardness} = S \times 0.5 \times \frac{1000}{V} \text{ ppm CaCO}_3$$

Here,

S = EDTA solution spent in titration, ml

V = the volume of the sample taken, ml.

For example, if 10 ml of 0.01 N EDTA solution was used in 50 ml of water sample,

$$\text{Total Hardness} = 10 \times 0.5 \times \frac{1000}{50} = 100 \text{ ppm CaCO}_3$$

located. 100 ppm CaCO_3 10 FS°. Then 50 ml of water is spent for the sample. The volume of 0.01 N EDTA solution as ml gives the total hardness directly as FS°.

1.7. DETERMINATION OF ACIDITY

The pH of natural waters is usually between 7-8. The water-soluble carbon dioxide causes the water to decrease in pH by forming carbonic acid. Furthermore, the hydrolysis of ions such as iron and aluminum in water may decrease the pH.

The acidity of the water (acidity) can also be found by titration with sodium hydroxide solution. Alkaline acidity can also be found in water.

1.7.1. Solutions to be used

1- 0.02 N standard sodium hydroxide solution:

Take 20 ml of the previously prepared 1 N NaOH solution and make up to 1 liter with distilled water without carbon dioxide.

2- Phenolphthalein indicator solution:

5 g of phenol is dissolved in a small amount of distilled water to 1 liter.

1.7.2. Experimental Procedure

A sample of 100ml of water is taken. Add 3-5 drops of phenolphthalein indicator. If a purple color is formed, the acidity of the water is zero. (This indicates that the pH of the water is greater than 8.3 and there is carbonate ion in the water.)

To determine the acidity in water if no color occurs when the phenolphthalein indicator is introduced, titrate with 0.02 N NaOH solution until a slight purple color is formed

1.7.2. Calculation

The acidity value of water is calculated as ppm CaCO_3 by the following correlation.

$$\text{acidity} = \frac{S \times N \times 50 \times 1000}{V} \text{ ppm CaCO}_3$$

Here, S = 0.02 N sodium hydroxide solution spent on titration, ml

N = Sodium hydroxide normality,

V = Sample volume, ml

For example, get 1 ml of a 0.02 N NaOH solution in a 100 ml water sample.

$$\text{acidity} = 1 \times 0.02 \times 50 \times \frac{1000}{100} = 10 \text{ ppm CaCO}_3$$

1.8. DETERMINATION OF CHLORIDE (MOHR METHOD)

In natural waters there is always some chloride ions. Chloride ion in surface waters is higher than groundwater. Sea water contains about 20 grams of chloride per liter.

The chloride ion in water is determined by titration with a silver nitrate solution.

1.8.1. Solutions to be used

1- 0.0141 N Silver nitrate solution:

2.396 g of silver nitrate is distilled off and dissolved in 1000 ml. This solution is equivalent to 1 ml = 0.5 mg chloride. Sodium chloride solution is used to adjust the solution.

2- 5% Potassium chromate indicator solution:

5 g of potassium chromate are dissolved in distilled water. To this solution is added silver nitrate solution until a slight reddish precipitate is formed. Allow to stand for at least 12 hours and then complete by filtration to 100 ml.

3- Standard sodium chloride solution:

Pure sodium chloride is dried in a 9000C oven for 1.5 hours. After cooling, we weigh 0.8243 g of NaCl. It is dissolved in a small amount of water and is completed in 1 liter. 1 ml of this solution corresponds to 0.5 mg of chloride.

1.8.2. Experimental Procedure

50 ml of water is taken. 0.5 ml of potassium chromate indicator solution is added. Initially, the solution takes a light yellow color. With 0.0141 N of silver nitrate solution, color is titrated from yellow to tile red.

1.8.3. Calculation

Chloride in water is calculated by the following correlation.

$$\text{Chloride} = S \times N \times 35.5 \times \frac{1000}{V} \text{ mg/l}$$

Here, S = 0.0141 N silver nitrate solution, ml

N = Silver nitrate solution normality

V = Sample volume taken, ml

For example, if 2 ml of 0.0141 N silver nitrate solution is consumed for 50 ml, the chloride concentration is calculated as follows.

$$\text{Chloride} = 2 \times 0.0141 \times 35.5 \times \frac{1000}{50} = 20 \text{ ppm Cl}^-$$

1.9. DETERMINATION OF ORGANIC SUBSTANCES (ACIDIC PERMANGANATE METHOD)

The amount of oxygen required for the chemical breakdown of organic compounds in water can be determined experimentally. For this purpose, organic compounds in water are reacted with acidic permanganate solution. The remainder of the permanganate is determined by the back titration method. Thus, the amount of permanganate that has been used to break down the organic compounds found in water is found.

1.9.1. Solutions to be used

1- Dilute sulfuric acid solution (1 + 3):

One volume of concentrated sulfuric acid and 3 volumes of distilled water are mixed.

2- 0.0125 N Potassium permanganate solution:

0.395 g of potassium peroxide is dissolved in a small amount of water to complete a liter of distilled water. This solution is adjusted to 0.0125 ammonium oxalate solution. 1 ml of this solution corresponds to 0.1 mg oxygen.

3- 0.0125 N Ammonium oxalate solution:

0.8882 g of ammonium oxalate $[(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}]$ is dissolved in a small amount of distilled water to a liter. This solution is used to adjust the permanganate solution.

1.9.2. Experimental Procedure

5 ml of dilute sulfuric acid solution is taken up in 50 ml of water. If water is a clean water, 10 ml of 0.0125 N potassium permanganate solution is added. (50 ml of potassium permanganate solution is suitable because the amount of organic matter is high in the polluted waters).

The sample is allowed to stand on the boiling water bath for half an hour. At the end of this period, some of the potassium permanganate contained in the sample was spent to break down organic compounds. (The excess of potassium permanganate must be left in the sample held for half an hour, which means that the solution is purple).

The amount of potassium permanganate solution remaining in the sample is determined by adding ammonium oxalate solution and back titration. Add 10 ml of 0.0125 N ammonium oxalate to the sample while it is still in hot state. (After this process, the purple color of the solution should be completely lost. Otherwise, ammonium oxalate solution should be added again.)

A portion of the ammonium oxalate which is added to the sample is consumed for the remaining potassium permanganate, and the remaining ammonium oxalate is determined by titration with potassium permanganate solution.

1.9.3. Calculation

The potassium permanganate solution, which was initially used in the sample, and the ammonium oxalate solutions used for back titration were taken to equal volume. If this permanganate consumption is (S) ml, the amount of organic matter in water is calculated as mg / l oxygen.

$$\text{Organic matter} = S \times 0.1 \times \frac{1000}{V} \text{ mg / oksigen}$$

Here, S = 0.0125 N potassium permanganate solution for titration, ml

V = sample volume taken, ml

For example, take 50 ml of water sample and get 2 ml of 0.0125 N Potassium permanganate for this

$$\text{Organic Matter} = 2 \times 0.1 \times \frac{1000}{50} = 4 \text{ mgO}_2 / \text{liter}$$

1:10. AMONIUM DETERMINATION

Ammonium salts in water can be determined colorimetric with Nessler marker. This reagent creates a characteristic red color with ammonium salts.

1.10.1. Solutions to be used

1- Distilled water without ammonia:

The distilled water is distilled off in a glass flask by adding KMnO_4 and Ca(OH)_2 in distilled water. Thus, impurities such as ammonia and carbonic acid, which can be found in normal distilled water, are completely removed.

2- Nessler Token:

10 g of anhydrous mercury-II iodide is crushed in a porcelain mortar with 5 g KI. Dissolve in small amounts of distilled water without ammonia. To this solution is added a cold solution of 20 g of sodium hydroxide dissolved in ammonia-free water. 100 ml of ammonia-free distilled water.

This marker is stored in a dark, well-lit color bottle.

3- Potassium-sodium tartrate solution:

Weigh 100 g of potassium-sodium tartrate (senyet salt). Dissolve in 200 ml of distilled water without ammonia. To this solution is added 100 ml Nessler reagent. After two to three days, a clear, clear solution is obtained.

1.10.2. Experimental Procedure

Take 50 ml of water to be analyzed. Add 1 ml of potassium - sodium tartrate solution and mix. Then 1 ml Nessler attends the reagent. If there is ammonia in the water, a color ranging from yellow to red occurs. Wait 10 minutes for the color to form completely.

The same process is carried out using ammonia-free distilled water instead of sample. This solution is used as a witness test.

Both samples are put into a colorimeter and compared with Nessler color discs. These discs have yellow to red colors and corresponding ammonia concentrations. The nearest value that matches the color of the solution is read. The result is given as mg / liter ammonia nitrogen.

1:11. IRON DETERMINATION (PHENANTHROLINE METHOD)

The iron +2 ion forms an orange complex with 1-10 of the phenanthroline solution. This color can be determined with the help of iron found in water. However, the water is boiled with hydroxyl amine in acidic medium to ensure that all iron (+2) contained in the solution becomes valuable.

1.11.1. Reagents

All reagents used should not contain iron ions. Degraded distilled water is used in the experiments.

1- Hydrochloric acid:

35% concentrated hydrochloric acid

2- Hydroxyl amine hydrochloride solution:

10 g of hydroxylamine hydrochloride $[\text{NH}_2\text{OH}.\text{HCl}]$ are dissolved in 100 ml of distilled water.

3- Sodium acetate solution:

350 g of sodium acetate $[\text{NaCH}_3\text{COO}.\text{H}_2\text{O}]$ are dissolved in 500 ml of distilled water and completed to one liter. 2 ml of concentrated hydrochloric acid is added to 100 ml of distilled water. To this end, 10 ml of sodium acetate solution is added to raise the pH of the solution obtained to 3.2-3.3.

4- Phenanthroline solution:

We weigh 0.120 g of 1-10 phenanthroline monohydrate $\text{C}_{12}\text{H}_8\text{N}_2.\text{H}_2\text{O}$. It is dissolved in 100 ml distilled water. To achieve this, it must be heated to 80 °C by mixing. (It is inconvenient to boil the solution)

5- Stock iron solution.

Weigh 1.404 g of iron-2 ammonium sulfate $[\text{Fe}(\text{NH}_4)_2.6\text{H}_2\text{O}]$. Dissolve by adding 50 ml of distilled water and 20 ml of concentrated sulfuric acid. 0.1 N KMnO_4 is added dropwise until a light pink color occurs on this solution. A liter of distilled water is completed. This solution contains 1 ml = 0.2 mg +2 ions.

6- Standard iron solutions:

These solutions are prepared on the day of use. Take 5, 10, 20, 30, 50 ml of the stock iron solution and make up to one liter with distilled water. Thus, standard solutions containing 1 mg / l-10 mg / l iron+2 ion are prepared.

1.11.2. Experimental Procedure

A 50 ml of water sample is taken and placed in a 125 ml solution, 2 ml of concentrated hydrochloric acid and 1 ml of hydroxyl amine are added. It is heated until boiling. All iron is transformed into Fe^{+2} . Boil until the volume is 15-20 ml, the solution is cooled to room temperature. 50 ml balloon is taken into the cup. Add 10 ml of sodium acetate buffer solution and 2 ml of phenantroline solution. 50 ml of distilled water is completed. Wait 10 minutes for full color development. Transfer to the Nessler tube.

Colorimetric designation:

A series of Nessler tubes are prepared in the same experiment using standard iron solutions of Fe^{+2} concentration. The color obtained by the sample is found by comparing with the color closest to the color. Thus, 50 mg of Fe^{+2} contained in the sample is determined.

1.11.3. Calculation

The amount of buffer iron present in water is calculated by the following correlation.

$$\text{Total Iron} = \frac{m \times 1000}{V}$$

Here, m = iron measured in the test sample, mg

V = Sample volume, ml.

1.12. DETERGENT DETERMINATION (METHYLENE BLUE METHOD)

Alkyl benzene sulfonate (ABS) or anionic detergents containing alkyl form methylene blue to form a blue colored compound. This compound is also soluble in chloroform and is proportional to the intensity of color. The intensity of this color can be measured by a spectrophotometer at a wavelength of 652 nm. This method is suitable for measuring the amount of detergent in water containing 0.025-100 mg / l ABS.

1.12.1. Devices

1- Spectrophotometer

2- Separation funnel, 500 ml

1.12.2. Solutions

1- Standard alkyl benzene sulfonate solution

Weigh 1 g of pure ABS, dissolve in distilled water and complete in liters.

Thus, 10 ml of the prepared stock solution is prepared and completed to 1 liter. The standard solution thus prepared has 1 ml = 0.01 mg ABS.

2- Phenolphthalein solution:

5 g of phenolphthalein are dissolved in 500 ml of 90% ethyl alcohol and complete with 1 liter of distilled water.

3- 1 N sodium hydroxide solution:

Weigh 40 g of NaOH, dissolve in distilled water and make up to 1 liter.

4- 1 N Sulphuric acid solution:

28 ml of concentrated sulphuric acid is completed in 1 liter with distilled water.

5- Chloroform

6- Methylene blue solution:

0.1 g of methylene chloride are dissolved in 100 ml of distilled water. Taking 30 ml of this solution, 500 ml of distilled water are added with 6.8 ml of concentrated concentrated sulfuric acid, 50 g of mono sodium dihydrogen phosphate monohydrate $[\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}]$. It is mixed and completed to one liter.

7- Washing solution:

To 6.8 ml of distilled water is added 6.8 ml of concentrated sulfuric acid and 50 g of sodium dihydrogen phosphate monohydrate. It is mixed and completed into liters.

1.12.3. Experimental Procedure

First, a calibration curve is drawn using the samples with the ABS concentration known. For this purpose, each of the 10 separating funnels is sampled from the standard ABS solution in the following volumes in ml.

0.0, 1.0, 3.0, 5.0, 7.0, 9.0, 11.0, 13.0, 15.0, 20.0 ml

Separate the funnel with 100 ml of distilled water. These samples are applied to the following processes to read the absorption values of each spectrophotometer. These values are plotted against the concentration and the calibration curve is drawn.

Detergent Determination in Sample:

10 ml-100 ml water sample is taken by considering the estimated detergent concentration in water. The following operations are performed on this sample.

a- 3-5 drops of phenol ftalein on the water sample is made by alkaline with sodium hydroxide solution.

b- 10 ml of chloroform and 25 ml of methylene blue solution are added. Shake for 30 sec. Wait for the phases to separate.

c- The chloroform layer collected in the bottom is transferred to a second separating funnel. The tip of the first separating funnel is further extracted three times using a small amount of chloroform.

d- All the extracts are collected in the same separating funnel. Add 50 ml of washing solution to this separating funnel and agitate for 30 sec. After waiting for some time to separate the phases, the chloroform layer is taken up in a 100 ml flask. 10 ml of chloroform solution is washed twice and these washings are collected in the flask and are complete with chloroform to the marking line.

Measuring:

Chloroform is used as a sample in the spectrophotometer. The absorbance value is measured at a wavelength of 652 nm. From this value, the amount of ABS is determined by the calibration curve.

1:13. PHOSPHATE DETERMINATION

Dilute phosphate solutions give the ammonium molybdate compound in acidic medium. This compound forms a dark blue colored complex with the amino naphthal sulfonic acid. This color can be determined with the help of color phosphate in water.

1.13.1. Solutions

1- Sulfuric acid solution:

120 ml of concentrated sulfuric acid and 750 ml of distilled water are mixed. The cooled solution is completed with 1 liter of distilled water.

2- Acidic ammonium molybdate solution:

50 g of ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\cdot 4\text{H}_2\text{O}]$ are dissolved in 200 ml of distilled water. It is carefully cooled into 310 ml of concentrated sulfuric acid. It is then completed in 1 liter with distilled water.

3-Amino naphthalene sulfonic acid solution:

Weigh 0.5 g of 1-amino 2-naphthal-4 sulfonic acid reagent. 1 g anhydrous sodium sulfite (Na_2SO_3) is dissolved in 5 ml of water and the previously weighed reagent is added. 30 g of sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) are dissolved in 200 ml of distilled water. This solution is kept in well-sealed bottles and in the dark.

4- Potassium phosphate standard solution:

0.7164 g of potassium dihydrogen phosphate [KH_2PO_4] is dissolved in a small amount of water and is completed in 1 liter. At the moment of use, remove 100 ml of this solution and make up to 1 liter with distilled water. The resulting solution contains 1 ml = 0.05 mg PO_4 .

1.13.2. devices

This experiment is performed by spectrophotometer. The spectrophotometer operates at a wavelength of 725 nm.

1.13.3. Experimental Procedure

Put 50 ml of water into the Nessler tube. Add 1 drop of phenolphthalein solution. If a purple color is formed, a few drops of sulfuric acid are dropped until the color disappears. 10 ml of distilled water. Then add 10 ml of the amino naphthol sulfonic acid solution and complete with 100 ml of distilled water. You will wait exactly 10 minutes. This time

Preparation of the calibration curve:

10, 20, 30, 40, and 50 ml of the standard phosphate solution by taking the above-mentioned path (mg phosphate-reading value) is drawn in the calibration curve.

1.13.4. Calculation

The amount of phosphate is determined by the calibration graph from the value read from the spectrophotometer.

1:13. CHEMICAL OXYGEN NEEDS (COD) DETERMINATION

The amount of oxygen required to ensure the chemical decomposition of organic compounds in water is defined as chemical oxygen demand. This value is considered a good measure of the degree of pollution of the water. Potassium is a stronger oxidizer than dichromate permanganate. The aliphatic and aromatic compounds and the oxidizing organic compounds, such as pyridine, can be degraded by dichromate. Silver sulphate is used as catalyst to facilitate disintegration.

1.14.1. Solutions

1- Concentrated sulphuric acid

2- Silver sulfate crystal

3- Ferroin indicator solution: 1.485 g 1.10 Phenantroline monohydrate is dissolved in 0.695 g iron sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) distilled water, 100ml is completed.

4- 0.25 N Potassium dichromate solution:

Weigh 12.25 g of dried potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) for 2 hours in a 103 °C oven. It is dissolved in a small amount of distilled water and completed to 1 liter.

5- 0.1 N Ammonium-iron II sulfate solution:

98 g of ammonium iron II sulphate [$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$] are dissolved in a small amount of distilled water. 20 ml of concentrated sulfuric acid is added, cooled and completed to liter.

6- 0.025 N Potassium dichromate solution:

100 ml of the previously prepared 0.25 N Potassium dichromate solution is taken and completed to liter.

7- Ferroin Solution:

1.735 g of 1-10 Phenantroline dihydrate and 0.695 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ are dissolved in distilled water together with 100 ml.

1.14. 2. Experimental procedure

50 ml of water is taken into a 500 ml mouth flask, 50 ml of distilled water and 25 ml of 0.25 N standard potassium dichromate solution is placed. Carefully add 75 ml of concentrated sulfuric acid. 0.4 g of solid silver sulfate is added.

The balloon is connected to a back cooler. The solution is boiled for two hours. A few boiling glass beads should be placed in the balloon to ensure proper welding. After two hours of boiling, the flask is cooled, the reflux is washed with 25 ml of distilled water. (Most of the time you don't need to boil for 2 hours).

The solution in the flask is taken up in a 500 ml flask. The balloon is washed with distilled water. The solution is diluted to about 350 ml. The excess potassium dichromate in the solution is titrated with 0.1 N iron-ammonium sulfate solution. For this add 2-3 drops of Ferroin indicator solution to the solution. Initially, the color is green-blue. At the end of titration, the color is reddish blue.

The same procedure is repeated on a witness sample using 50 ml distilled water instead of the sample under the same conditions.

1.14.3. Calculation

Chemical oxygen demand is calculated with the following correlation in mg oxygen / liter.

$$\text{COD} = (A - B) \times N \times \frac{8000}{V} \text{ mg/l}$$

Here, A = 0.1 N iron ammonium sulphate solution spent for the witness sample

B = 0.1 N iron ammonium sulphate solution spent on the sample, ml

N = Iron ammonium sulphate solution normality

V = Sample volume, ml

1:15. DISSOLVED OXYGEN DETERMINATION (WINKES METHOD)

The oxygen dissolved in water oxidizes the manganese hydroxide in the alkaline solution to form the trivalent manganese hydroxide. When acid is added to the solution, manganese (3) hydroxide dissolves and reacts with iodide in the solution to give the free state iodine. This iodine is titrated with sodium thiosulphate solution. Thus, an equivalent amount of dissolved sodium thiosulphate solution is consumed.

1.15.1. Solutions

1- Manganese sulfate solution:

480 mg of manganese sulphate [$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$] is dissolved in distilled water and completed in liters.

2-Alkali iodide azide reagent:

500 g of sodium hydroxide and 135 g of sodium iodide (or 150 g of KI) are dissolved in distilled water and completed in liters. To this solution is added a solution of 10 g of sodium azide (NaNH_2) dissolved in 40 ml of distilled water.

3- Concentrated sulfuric acid (approx. 30 N)

4- Starch indicator solution:

5 g of soluble starch are slurried in a small amount of distilled water in a beaker. This slurry is poured into 1 liter of boiling water. Boil for a few minutes. Allow to settle overnight. The upper part is transferred to a bottle.

5- 0.1 N Stock sodium thiocyanate solution.

24.82 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ are dissolved and dissolved in chilled distilled water. 1 liter is completed.

6- 0.025 N Sodium thiocyanate solution:

Take 250 ml of stock sodium thiosulfate solution and make up to liter. 1 ml of this solution corresponds to 0.2 mg of dissolved oxygen.

7- 0.025 N Standard potassium dichromate solution:

Weigh 1.226 g of dried potassium dichromate for 2 hours at 103 °C. Slightly dissolve in water and complete in liters.

1.15.2. Experimental Procedure

The mouth of the 250 or 300 ml special BOI bottles with glass lid is filled with water sample. The bottle must be filled completely with water from the mouth. The cap of the bottle is closed so that no air bubbles are left in the bottle.

Then 2 ml of manganese sulphate solution and 2 ml of alkali iodide azide solutions are added to the flask with a long pipette opening to the bottom of the bottle. The cap of the bottle is closed again so that no air bubbles remain. The bottle is stirred for 30 seconds. Then wait for 10 minutes for the manganese hydroxide to precipitate. At the end of this period, the lid of the vial is opened, and 2 ml of concentrated sulfuric acid is placed into the lid with a pipette and the lid is closed again. The vial is stirred until all the precipitate is dissolved.

The solution in the vial is taken up in a flask. The flask is washed with a little distilled water. The washing water is added to the flask. The iodine in the solution is titrated with 0.025 N sodium thiosulphate solution until light yellow. Then add 1 ml starch indicator solution. Titration is continued until the blue color disappears.

1.15.3. Calculation

The amount of dissolved oxygen in the water sample is calculated as mg / l with the following correlation.

$$\text{Dissolved Oxygen} = A \times 0.2 \times \frac{1000}{B - C} \text{ mg / l}$$

Here, A = 0.025 N sodium thiosulfate solution used in titration, ml

B = BOD bottle used, ml

C = Total volume of reagents introduced into the vial during the experiment, ml

For example, suppose that a 300 ml BOD bottle is used and 12 ml of a 0.025 N sodium thiosulphate solution is spent.

$$\text{Dissolved Oxygen} = 12 \times 0.2 \times \frac{1000}{300 - 6} = 8.2 \text{ mg / l}$$

BIOCHEMICAL OXYGEN NEEDS (BOD)

The amount of oxygen required to break down organic matter in water by biochemical reactions is defined as biochemical oxygen demand. The need for biochemical oxygen is usually measured at 20° C for a period of 5 days. BOD₅ value gives a good idea about the organic pollution of water. The general principle of the experiment was to determine the amount of oxygen spent in this period by measuring the dissolved oxygen contained in water at the beginning and after 5 days of incubation at 20 °C. Oxygen consumption is carried out by microorganisms in the environment.

1.16.1. Reagents

1- Manganese sulfate solution:

480 g of manganese sulphate [MnSO₄.4H₂O] is dissolved in a small amount of distilled water and completed in liters.

2 - Alkali iodide azide solution:

500 g of sodium hydroxide and 135 g of sodium iodide (or 150 g of potassium iodide) are dissolved in distilled water and completed in 1 liter. To this solution is added azide solution prepared by dissolving 10 g of sodium nitrogen (NaN₃) in 40 ml of distilled water.

3- Sulfuric acid solution:

4- 0.025 N sodium Thiosulfate solution:

6.205 g of sodium thiosulfate [Na₂S₂O₃.5H₂O] are dissolved in boiled distilled water and completed to 1 liter. 1 ml of this solution corresponds to 0.2 mg oxygen.

5- 0.025 N standard sodium dichromate solution:

1.226 g of dry potassium dichromate are dissolved in a small amount of distilled water and completed to 1 liter.

6- Starch indicator solution:

5 g of soluble starch are slurried in a small amount of water in a beaker. This slurry is poured into 1 liter of boiling water. Boil for a few minutes. Allow to settle overnight. Dry starch solution in the upper part is transferred to a bottle.

7- Preparation of dilution water:

Dilution water is prepared by mixing each of the following solutions in appropriate proportions.

a) phosphate buffer solution:

8.5 g of potassium dihydrogen phosphate [KH_2PO_4], 24.75 g of dipotassium hydrogen phosphate [K_2HPO_4], 33.4 g of disodium hydrogen phosphate [$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$] and 1.7 g of ammonium chloride are dissolved in about 500 ml of distilled water to complete the liter. $\text{PH} = 7.2$ in this solution.

b) Magnesium sulfate solution:

22.5 g magnesium sulfate [$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$] is dissolved in a small amount of distilled water and is completed in 1 liter.

c) Calcium chloride solution:

27.5 g of anhydride calcium chloride is dissolved in a small amount of distilled water and completed to 1 liter.

d) Iron III Chloride solution:

0.25 iron III chloride [$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$] is dissolved in a small amount of distilled water and completed to 1 liter.

Dilution water is prepared as follows:

One ml of each of the four solutions prepared as described above on 1 liter of distilled water is added. The temperature is around 20°C . At this temperature, air is passed through the water and saturated with oxygen and kept in the incubator at 20°C for at least 12 hours. It is appropriate to dilute the dilution water with a small amount of contaminated water.

Approximately 8 mg / L of dissolved oxygen should be present in the dilution water ready for use.

Dilution Ratio:

In this experiment, it is very important to predict the ratio of contaminated water and dilution water. If a sufficient amount of dilution water is not used, no oxygen is left in the sample at the end of the five-day incubation period and the result is not obtained. the value will be insensitive.

The dilution rate can be selected as follows depending on the BOD_5 value of the water subjected to the experiment.

Estimated BOD_5 value of water	Water sample volume for 300 ml BOD
500 mg/l	1 ml
100 mg/l	5 ml

50 mg/l	10 ml
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1.16.2. Experimental Procedure

4 items BOD bottles are used to determine the BOD₅ value of a polluted water. Two of these bottles contain contaminated water + dilution water, while the other two contain only dilution water.

Fill up to half of the 300 ml BOD bottle with dilution water. Add a pre-calculated amount of contaminated water with the help of a pipette. The bottle is filled with dilution water up to the mouth, the lid is closed.

Only one of the two vials prepared with sample water with dilution water is placed in the incubator at 20 °C. It is kept at constant temperature for five days.

In the remaining two flasks, dissolved oxygen amounts are determined to determine the initial values. At the end of the fifth day, in the bottles removed from the incubator, similar amounts of dissolved oxygen for five days are determined.

1.16.3. Calculation

The BOD₅ value is calculated in mg / L with the following correlation.

$$BOD_5 = \frac{[DO_i - DO_{final}]_{\text{sample}} - [DO_i - DO_{final}]_{\text{Dilution water}}}{\text{Dilution ratio}}$$

For example, 5 ml of a 300 ml BOD flask was placed and the dissolved oxygen values were found as follows.

Example DO_i = 7.8 mg / l

DO_{final} = 3.4 mg / l

Dilution water = DO_i = 7.9 mg / l

$$DO_{\text{final}} = 7.8 \text{ mg / l}$$

$$BOD_5 = \frac{(7.8 - 3.4) - (7.9 - 7.8)}{5 / 300}$$

$$BOD_5 = 258 \text{ mg / l}$$

1:17. DETERMINATION OF SOLID MATERIALS

1 liter of water is mixed with a well mixed with a tromp from a Gooch crucible is filtered. The suspended solids remain on the crucible. The crucible is dried in a 105 °C oven, cooled and weighed. The difference between the scales of the scallop and the empty scales is the suspended material. In order to determine the volatile solids contained in these solids, the crucible is again placed in a 400 ° C oven. Here, all organic compounds contained in the solids are broken down, the crucible is cooled and weighed. Weight loss is given in mg / l as suspended solids.

1:18. DETERMINATION OF SETTLEABLE SOLID MATERIALS

The IMHOFF funnel is used to determine the solids in the water that can collapse. One liter of water is collected by mixing into the imhoof funnel. Hold the funnel for 30 minutes. The volume of suspended substances in water is read in ml at the marked area at the bottom of the imhoff funnel. The result is given as solid solids.