

[4] COLOR IN WATER

olor in water is the result of dissolved extracts from metals in rocks and soil, from organic matter in soil and plants, and occasionally from industrial by-products. When color is caused by metals, it is usually due to iron, copper, or manganese ions in the water. Leaves and peat may add tannin glucosides and their derivatives to

water. Leaves and peat may add tannin, glucosides, and their derivatives to the water, resulting in a yellow or brown hue. Industries can add a variety of chemicals with various colors.

In water and wastewater treatment, we make a distinction between true color and apparent color. **True color** is the result of dissolved organics, minerals, or chemicals in water, as noted above. When testing the color of a water sample, the goal is to measure the true color of the water. However, suspended materials in the water (turbidity) can change the **apparent color** of the water (the color of the water before filtration.) As a result, the first step of measuring true color is to remove the water's turbidity by filtration or centrifugation.

You should also be aware that changes in pH can change the true color of water. As a result, pH is always measured along with color during color testing.

Measuring Color

Two types of procedures can be used to measure the color in water - the visual method or the instrumental method.

The visual method is the simplest since it consists of a water sample being compared to a series of colored slides or tubes. This method can be used in most cases, but it is not appropriate for use on water which has been contaminated by industrial wastes. Various instrumental methods can be used to create a more accurate portrayal of the water's color if the color cannot be matched using the visual method.

When using the visual method, color is usually measured in color units. Water with color as high as 20 units will not ordinarily be noticed by the consumer, but the water plant should be operated so that the color will be less than 20 units.



Treating Color

Color in water is nearly always harmless. However, for aesthetic reasons, color in water should be maintained at an unnoticeable level. A plant will have little difficulty in producing an effluent with color of 10 units or less since coagulation followed by chlorination or ozonation tends to remove the majority of the color from water.

Lab Procedures

For any color testing method, the first step will be to remove turbidity, so we will describe this procedure first. Then we will briefly introduce two different visual methods and one instrumental method used for measuring color. All of these methods are treated in much greater depth in Standard Methods.

Removing Turbidity

Before testing for color, you must remove the turbidity from the water. Removal of suspended matter by centrifuging has been found to give the best results. Although filtration will remove suspended matter, it also tends to change the true color of the water.

A. The Platinum-Cobalt Method

The standard method used for measuring color is a visual method known as the Platinum-Cobalt Method. In the Platinum-Cobalt method, color is measured by comparison of the sample to standards prepared with various concentrations of potassium chloroplatinate and cobaltous chloride. Both the sample tube and the standards are viewed against a white background and the standard tube closest in color to the sample is chosen.

B. Comparison with Glass Discs

The Platinum-Cobalt method is not well adapted for field work, so water is sometimes tested by comparing the sample to glass discs. These discs are produced by various laboratory supply companies in a series of hues, calibrated to correspond to colors on the platinum scale.

When using this method, the glass discs are held at the end of metallic tubes. The operator views the discs through the tubes while looking toward a white surface. The disc which most closely matches the color of the sample gives the number of color units found in the sample water.

C. Instrumental Methods



<u>Time required:</u>

An hour or less depending on the number of samples determined.

Equipment:

- Color standards
- Empty vial to hold the samples
- Clean and dry wipe

Significant Experimental Hazards

• Student should be aware of hazards associated with the use of all glassware (cuts.)

Procedure:

Issues to consider for your practical report

- What are the potential sources of error in this analytical determination? How could they be overcome?
- What are the alternative methods for determining the color of aqueous samples? How do they compare to this method?
- What are typical color values of water in Jordan? How do your data compare with these values? (Drinking, surface and ground water)
- What are the main sources of color in water and wastewater?
- What are the potential health and environmental effects if any of extreme color values?





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	Experiment (4): Color of Water
	Experimental Results
Name	Date
ID No.	Group



Observations & Calculations:





cidity is the measure of the capacity of water to naturalize bases. Strong mineral acids

[5] ACIDITY OF WATER

(such as sulfuric acid, hydrochloric and nitric acid), **Weak Acids** (such as carbonic acid and acetic acid) present in water samples contributes to the acidity of water.

Usually dissolved carbon dioxide (CO₂) is the major acidic component present in the unpolluted surface waters.

In ground waters and waters from hypolimnion of stratified lakes and reservoirs often contain considerable amounts of CO_2 ; this concentration results from bacterial oxidation of organic matter with which water has been in contact and under these conditions the CO_2 is not free to escape to atmosphere.

Mineral acidity is present in many industrial waste particularly, those of the metallurgical industry and some



from the production of synthetic organic materials. The drainage from abandoned mines and lean ore dump, will contain significant amounts of sulfuric acids or salts of sulfuric acid if sulfur, sulfides or iron pyrites are present

Salts of heavy metals hydrolyzes in water to release mineral acidity (particularly with trivalent metal ions)

Combustion of fossil fuels in power plants and automobiles leads to the formation of oxides of nitrogen and sulfur, which when mixed with rain hydrolyze to form sulfuric acid and nitric acids. The resulting acid rain can lower the pH in poorly buffered lakes and adversely affecting the aquatic life and can increase the amount of chemicals, such as aluminum, leaching from soli into surface runoff.

For these reasons control has been placed on the amount of sulfur and nitrogen oxides, that can be discharged to the atmosphere through combustion.



Basically there are two types of acidity; total acidity (Phenolphthalein acidity) and mineral acidity (Methyl Orange acidity).

Mineral acidity (M.O): It has to do with the presence of strong mineral acids, it is measured by titration to a pH of about 3.5 (the Methyl Orange end point) since its' neutralization is essentially completed at that pH.

Total acidity (**Ph.Ph**): It is measured by titration to a pH of 8.3; which is the phenolphthalein end point. The reason for choosing that pH is that the stoichiomatric end point for carbonic acid is not reached until the pH has been raised above 8.5; due to that it is customary to consider that all waters having a pH lower than 8.5 contain acidity.

The importance of measuring the acidity is due to:

- 1. Acidity interferes in the treatment of water. Carbon dioxide is of important considerations in determining whether removal by aeration or simple neutralization with lime/lime soda ash or sodium hydroxide will be chosen as the water treatment method.
- 2. The size of the equipment, chemical requirements, storage spaces and cost of the treatment all depend on the carbon dioxide present.
- 3. High acidity of water is not used for construction purposes. Especially in reinforced concrete construction due to the corrosive nature of high acidity water.
- 4. Water containing mineral acidity is not fit for drinking purposes.
- 5. Industrial wastewaters containing high mineral acidity must be neutralized before they are subjected to biological treatment or direct discharge to water source.

Principle of measurement:

Titration with standard reagent will be used to determine the acidity. When sodium hydroxide is used the reaction involved in the neutralization maybe considered to occur into steps:

 $2 \text{ NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$

 $Na_2CO3 + CO_2 + H_2O \rightarrow 2 \ NaHCO_3$

<u>Time Required</u>

Two hours, depending upon the number of water samples determined



Equipment:

- 1. 250 ml conical flasks
- 2. 100 ml cylinder
- 3. 50 ml burette
- 4. Boss, clamp, retort stand and white tile

Reagents:

- 1. Sodium hydroxide (NaOH)
- 2. Methyl orange indicator
- 3. Pheolphthaline indicator
- 4. Suitable water samples (e.g. Tap, lake or river waters)

Significant Experimental Hazards

- Student should be aware of hazards associated with the use of all glassware (cuts).
- Sodium hydroxide is very hazardous in case of skin contact (corrosive, irritant), of eye contact (irritant, corrosive), of ingestion, of inhalation. The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering.
- Methyl orange is hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Severe over-exposure can result in death.
- Phenolphthalein indicator is Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion. It may also stain clothing and skin.

Procedure:

A. Mineral Acidity (M.O Acidity)

- (1) Rinse the burette with NaOH (titrant) and then discard the solution.
- (2) Fill the burette with 0.02 M NaOH.
- (3) Pour 100 ml of water sample into 250 ml conical flask.
- (4) Add a few drops of methyl orange mix indicator (max. 3 drops) to the sample, the color changes to *YELLOW*.
- (5) Titrate the sample with NaOH solution until the orange color faints and turns to *BLUE*.
- (6) Repeat this rough titration at least twice more, or until two concordant results are obtained. (the standard deviation need to be less than 15%)



B. Total Acidity (Ph.Ph. Acidity)

- (1) Use the same burette and titrant of the 1^{st} part.
- (2) Pour 100 ml of water sample into 250 ml conical flask.
- (3) Add a few drops of phenolphthalein indicator (3 drops) to the sample, the color should remain colorless. (if all the acidity present is mineral the color directly will be pink)
- (4) Titrate the sample with NaOH solution until the color changes to faint pink.
- (5) Repeat this rough titration at least twice more, or until two concordant results are obtained.

Calculation

Mineral Acidity (mg/l) =	Volume of NaOH (ml) ×NaOH Molarity (M)×50×1000
(M.O Acidity)	Volume of the sample (ml)

Total Acidity $(mg/l) =$	Volume of NaOH (ml)×NaOH Molarity (M)×50×1000
(FILFII Acidity)	Volume of the sample (ml)

Issues to consider for your practical report

- What are the potential sources of error in this experiment? How could they be overcome φ ?
- Are there alternative methods for determining the acidity of water? If so, how do they compare to this method?
- What is the source of the Unknown River and lake samples acidity?
- What are typical water acidity values in rivers, streams, swimming pods and drinking water in Jordan? How do your data compare with these values?
- How can acidity be removed for domestic and industrial purposes?
- What are the legal limits (if any) of acidity in drinking water? Do your values exceed such legal limits?
- What are the potential human health and environmental effects (if any) of excess acidity in potable water?



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	Experiment (5): Acidity of Water
	Experimental Results
Name	Date
ID No.	Group

NaOH (M	ſ)			Indicator _		
Sample	Volume of	Burette R	Reading	Volume of	Observation	Standard
ID	Sample (ml)	Initial	Final	NaOH (ml)	(color change)	Deviation
		(
Fotal NaOH (M	Acidity [)			Indicator		
Fotal NaOH (M Sample	Acidity [) Volume of	Burette R	Reading	Indicator	Observation	Standard
Fotal NaOH (M Sample ID	Acidity [) Volume of Sample (ml)	Burette R Initial	Ceading Final	Indicator	Observation (color change)	Standard Deviation
Fotal NaOH (M Sample ID	Acidity [) Volume of Sample (ml)	Burette R Initial	Reading Final	Indicator Volume of NaOH (ml)	Observation (color change)	Standard Deviation
Fotal NaOH (M Sample ID	Acidity [) Volume of Sample (ml)	Burette R Initial	Reading Final	Indicator	Observation (color change)	Standard Deviation
Fotal NaOH (M Sample ID	Acidity [) Volume of Sample (ml)	Burette R Initial	Reading Final	Indicator	Observation (color change)	Standard Deviation
Fotal NaOH (M Sample ID	Acidity I) Volume of Sample (ml)	Burette R Initial	Reading Final	Indicator	Observation (color change)	Standard Deviation
Fotal NaOH (M Sample ID	Acidity I) Volume of Sample (ml)	Burette R Initial	Ceading Final	Indicator	Observation (color change)	Standard Deviation
Fotal NaOH (M Sample ID	Acidity I) Volume of Sample (ml)	Burette R Initial	Reading Final	Indicator Volume of NaOH (ml)	Observation (color change)	Standard
Fotal NaOH (M Sample ID	Acidity I) Volume of Sample (ml)	Burette R Initial	Reading Final	Indicator Volume of NaOH (ml)	Observation (color change)	Standard Deviation
Fotal NaOH (M Sample ID	Acidity I) Volume of Sample (ml)	Burette R Initial	Keading Final Image: State St	Indicator Volume of NaOH (ml)	Observation (color change) Image: Color change Image: Col	Standard Deviation



Observations & Calculations:





[6] ALKALINITY_OF_WATER

kalinity of water is a measure of its capacity to

neutralize acid. The difference between a base and an alkali is in the structure. Alkali is free OH- ions that neutralize the solution initially, but then as more solution is added, it becomes alkaline. A base is a molecule that does not add more OH- ion into the solution, but removes H+ ions, making the solution basic. In practice alkalinity may be determined by measuring the number of moles of H^+ required to titrate one liter of water sample to the end point. Alkalinity is therefore a useful measure of the capacity of water to resist acidification from acid precipitation. The presence of carbonate, bicarbonate and hydroxide ions impart the alkalinity of natural or treated waters.

Total Alkalinity (mol/l) = $2[CO_3^{2^-}] + [HCO_3^-] + [OH^-] - [H^+]$(5.1)

In natural waters (pH \approx 7), the hydroxide ions and the hydrogen ion will be the same, so they will be neglected in the calculations associated with this experiment.

Determining the carbonate and bicarbonate ions in each other's presence is often important in environmental chemistry. The equations below shows the reactions involing them

> a) $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ b) $H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$ c) $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$

Initially, the water sample will contain both carbonate and bicarbonate ions and will be alkaline. The addition of acid to the water sample will convert carbonate to bicarbonate until no more carbonate remains. The addition of further acid will convert the bicarbonate to carbonic acid until no more bicarbonate remains. The carbonate and carbonic acid equivalence points may be determined either by titration using indicators or by pH titration. Hence in our experiment we will use the indicator method.

Phenolphthalein Alkalinity

Phenolphthalein, an indicator that produces a color change in the pH range 8.3-10, enables the measurement of the alkalinity fraction contributed by the carbonate ion. The end point determined with this indicator represents the completion (equivalence point or stiochiometric end point) of the following reaction:



$$2H^+(aq) + CO_3^{2-}(aq) \rightleftharpoons H_2CO_3(aq)$$
(5.2)

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NOTE : half of the carbonate has been neutralized by the acid forming bicarbonate ions. This is sometimes referred to as the phenolphthalein alkalinity.

Phenolphthalein alkalinity (Ph.Ph Alk.) = $[CO_3^{2^-}]_{actual}/2$ (5.3)

Methyl Orange Alkalinity

Methyl orange indicator responds in the pH range 3.2-4.5, and may therefore be used to assess the alkalinity due to carbonate and bicarbonate. At this pH, all of the bicarbonate ions initially present in water sample, together with all of those produced from the half-reaction of the carbonate ions, will be neutralized. The resulting alkalinity is known as the total alkalinity.

$$HCO_3^{-}(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g) \dots (5.4)$$

(Estimated) Total alkalinity = $2[CO_3^{2^-}] + [HCO_3^-]$(5.5)

The importance of the carbonate/bicarbonate system in natural waters stems from their ability to act as buffers in natural waters. The oceans are described as being buffered since relatively large quantities of acid or base can be added to sea water without causing much change to its pH. However, many freshwater lakes do not have a large buffer capacity and consequently a small addition of acid (e.g. from acid precipitation or industrial effluent) can cause large changes in pH without warning.

The phenolphthalein alkalinity and the total alkalinity are useful for the calculation of chemical dosages required in the treatment of natural water supplies.

Time Required

Two hours, depending upon the number of water samples determined. (Assuming all reagents is made up in advance).

Equipment:

- 1. 250 ml Erlenmeyer flasks
- 2. 100 ml volumetric cylinder
- 3. 50 ml burette
- 4. Boss, clamp, retort stand and white tile.



Reagents:

- (1) Phenolphthalein indicator
- (2) Methyl orange indicator
- (3) Hydrochloric acid (HCl) solution

Significant Experimental Hazards

- Student should be aware of hazards associated with the use of all glassware (cuts.
- Hydrochloric acid is harmful by digestion and may cause severe burns to eye and skin.
- Phenolphthalein indicator maybe harmful if ingested in quantity and may irritate eyes and skin.
- Methyl orange indicator maybe harmful if ingested in quantity and may irritate eyes and skin. It may also stain clothing and skin.

Procedure:

Part A: Ph. Ph alkalinity (carbonate alkalinity)

- (1) Clean the burette then fill it with HCl solution
- (2) Measure 100 ml of the sample in to a 250 ml Erlenmeyer flask.
- (3) Add 3 drops of phenolphthalein indicator.
- (4) Titrate the solution with HCl until the indicator color changes from pink to colorless. <u>REMEMBER</u> The volume of the acid used (Carbonate/ph.ph. Alk.) <u>corresponds to half of the actual carbonate present.</u>
- (5) Repeat this rough titration at least twice more, or until two concordant results are obtained. (SD should be less than 10%)

Part B: M.O. alkalinity (total alkalinity)

- (6) Measure 100 ml of the sample into a 250 ml Erlenmeyer flask.
- (7) Add a few drops of methyl orange indicator.
- (8) Titrate the solution with 0.100 M HCl until the indicator color changes from yellow to red. The volume of the acid used (Total alkalinity/M.O. alkalinity) corresponds to the sum of the carbonate and bicarbonate present in the aqueous solution.
- (9) Repeat this rough titration at least twice more, or until two concordant results are obtained. (SD should be less than 10%)



Calculation



Issues to consider for your practical report

- What are the legal limits (if any) of alkalinity in drinking water? Identify other ions that could make a minor contribution to the alkalinity of natural waters.
- How can the pH of natural waters be restored once their buffering capacity has been exceeded and they have become acidified?
- Are there other methods that can determine the alkalinity in water samples?
- What are typical phenolphthalein and total alkalinity values for rivers, streams and drinking water in Jordan or the world? How do your data compare with these values?
- What are the potential sources of error in this analytical determination? How could they be overcome?
- Compare your results with the legal limits; do your values exceed such legal limits?
- Assume that your sample alkalinity had exceeded the maximum legal limits, how can you treat such water and reduce its alkalinity to be within the legal limits?

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	Experiment (6): Alkalinity of Water
	Experimental Results
Name	Date
ID No.	Group

HCI(M)				Indicator	-	
Sample	Volume of	Burette R	eading	Volume of HCl	Observation	Standard
ID	Sample (ml)	Initial	Final	(ml)	(color change)	Deviation
Fotal	Alkalinit	y				
Fotal HCl(M) _ Sample	Alkalinit	y Burette R	eading	Indicator	Observation	Standard
Fotal HCl(M) _ Sample ID	Alkalinit Volume of Sample (ml)	y Burette R Initial	eading Final	Indicator Volume of HCl (ml)	Observation (color change)	Standard
Fotal HCl(M) _ Sample ID	Alkalinit	y Burette R Initial	eading Final	Indicator Volume of HCl (ml)	Observation (color change)	Standard Deviation
Fotal HCl(M) _ Sample ID	Alkalinit Volume of Sample (ml)	y Burette R Initial	eading Final	Indicator Volume of HCl (ml)	Observation (color change)	Standard Deviation
Fotal HCl(M) _ Sample ID	Alkalinit Volume of Sample (ml)	y Burette R Initial	eading Final	Indicator Volume of HCl (ml)	Observation (color change)	Standard
Fotal HCl(M) _ Sample ID	Alkalinit Volume of Sample (ml)	y Burette R Initial	eading Final	Indicator Volume of HCl (ml)	Observation (color change)	Standard Deviation
Fotal HCl(M) _ Sample ID	Alkalinit	y Burette R Initial	eading Final	Indicator Volume of HCl (ml)	Observation (color change)	Standard
Fotal HCl(M) _ Sample ID	Alkalinit	y Burette R Initial	eading Final	Indicator Volume of HCl (ml)	Observation (color change)	Standard Deviation
Fotal HCl(M) _ Sample ID	Alkalinit	y Burette R Initial	eading Final	Indicator Volume of HCl (ml)	Observation (color change)	Standard Deviation
Total HCl(M) _ Sample ID	Alkalinit	y Burette R Initial	eading Final	Indicator Volume of HCl (ml)	Observation (color change)	Standard Deviation



Observations & Calculations:



hloride (Cl⁻) is one of the major inorganic ions in water and wastewaters. In potable water, the saltiness is

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variable and dependent upon both the concentration of chloride ions and the presence of other ions (Na, K, Ca, Mg,...) . Waters containing 250 mg Cl⁻/l can taste salty if sodium ions are also present, and yet waters containing 1000 mg Cl⁻/l may not taste salty if the predominant cations present are calcium and magnesium. There are many potential sources for the chloride in natural and drinking waters and consequently its determination is important. The chloride concentration is higher in wastewater than in raw water because sodium chloride is a common article of diet and passes unchanged through the digestive system. Along the sea coast chloride may be present in high concentration because of leakage of salt water into the sewage system. . In addition, a high chloride contents may harm metallic pipes and structures as well as growing plants. One of analytical procedures to determine the chloride concentration is Mohr's titration.

The Mohr Method uses silver nitrate for titration (Normality: 0.0141) (method applicability: 0.15 to 10 mg/L chloride ions). This corresponds to 1 mL of 0.0141 equals to 1 mg chloride in solution. During the titration, chloride ion is precipitated as white silver chloride (Eq.1):

$AgNO_3 + XCl \leftrightarrow AgCl + XNO_3$(6.1)

The indicator (potassium chromate) is added to visualize the endpoint, demonstrating presence of excess silver ions. In the presence of excess silver ions, silver chromate forms a reddish-brown precipitate (Eq.2). This stage is taken as evidence that all chloride ions have been consumed and only excess silver ions have reacted with chromate ions:

$$2Ag^{+} + CrO4^{2-} \leftrightarrow Ag_2CrO_4....(6.2)$$

The reaction is potentially subject to interference that may limit its accuracy. Sulfate, thiosulfate and sulfide ions interfere with the reaction but maybe removed before measurement.

Time Required

Three hours, depending upon the number of water samples determined



Equipment:

- 1. 250 ml Erlenmeyer flasks
- 2. 50 ml burette
- 3. 100 ml measuring cylinder
- 4. Boss, clamp, retort stand and white tile and tongs

Reagents:

- 1. 0.0141 M silver nitrate (AgNO₃) solution
- 2. Potassium chromate (K₂CrO₄) solution (as indicator) in dispenser
- 3. Suitable water samples (e.g. tap, lake or river waters)

Significant Experimental Hazards

- Student should be aware of hazards associated with the use of all glassware (cuts) and fume cupboards.
- Silver nitrate may also color clothes and skin
- Potassium chromate indicator may be harmful if ingested in quantity and may irritate eyes and skin.

Procedure:

- (1) Measure 50 ml of blank sample into a 250 ml Erlenmeyer flask.
- (2) Add 1 ml of potassium chromate indicator from a dispenser. You must take great care to add the correct amount of indicator. If you add too much, silver nitrate will precipitate before the end point reached; if you add too little, formation of silver chloride is less distinct, thus making it difficult to see the end point.
- (3) Titrate the water sample with 0.0141 M silver nitrate solution. You should add the silver nitrate very slowly from the burette until the red color formed by each addition begins to disappear more slowly. This indicates that most of the chloride has been precipitated. Continue the titration until a faint but distinct color change .This faint reddish-brown color should persist after brisk shaking.
- (4) Carry out the same determination by using water (samples).
- (5) Repeat this rough titration at least twice more, or until two concordant results are obtained.



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Calculation

$$Cl^{-}mg/L = \frac{(A-B) \times Normality of titrant \times 35,450}{vol of sample}$$

$NaClmg/L = (mg Cl^{-}/L) \times 1.65$

Where

- A: volume of titrant used for the water sample
- B: volume of the titrant used for the blank (distilled water)

Issues to consider for your practical report

- What are the potential sources of error in this experiment? How could they be overcome?
- What are the potential human health and environmental effects (if any) of excess chloride in potable and natural waters?
- Identify alternative methods for determining chloride concentrations in water samples. What are their advantages/ disadvantages/ detection limits?
- What are typical chloride concentration for rivers, streams, lakes, swimming pools and drinking water in Jordan/World? Do your values exceed such legal limits?
- o Identify the main sources of chloride in natural waters?





	<u>Experiment (7): Chloride In Water</u> Experimental Results
Name	Date
ID No.	Group

Chlori	de						
AgNO ₃ (M							
Sample	Volume	Burette		Volume	Cl-mg/l	NaCl mg/l	Color change
D	of	Reading		of			
	Sample	Initial	Final	Titrant			
	(Iml)			(ml)			



Observations & Calculations:





Hard waters are the waters that requires a considerable amount of soap to produce a foam and also produces scale in hot water pipes,

[8] HARDNESS IN WATER

heaters, boilers and kettles. Hardness index is used by environmental chemists to measure the concentration of Ca^{2+} and Mg^{2+} ions in water. Chemically, the hardness index is defined as the sum of the concentration of Ca^{2+} and Mg^{2+} . Hardness is traditionally expressed as the mass (in mg) per liter of water calcium carbonate that contains the same number of dispositive (2+) ions.

Hardness types are :

(a) TEMPORARY HARDNESS

(b) **PERMANENT HARDNESS**

The most common type of hardness in water is **TEMPORARY HARDNESS**, caused by the presence of dissolved calcium and/or magnesium compounds. The main natural source of these salts is from rocks containing calcium or magnesium carbonate, such as limestone (CaCO₃) and dolomite (CaCO₃.MgCO₃).

Calcium carbonate is insoluble in water but reacts with carbon dioxide (which is easy soluble in water and is in plentiful supply from the atmosphere) to form calcium hydrogen carbonate (or bicarbonate), which is soluble in water. The chemical reaction that takes place is:

$CaCO_3 (s) + CO_2 (g) + H_2O (l) \rightleftharpoons Ca(HCO_3)_2 (aq) \dots (7.1)$

These dissolved salts cause the hardness of water. The reaction is reversible; on heating water that contains bicarbonates of calcium and magnesium, the bicarbonate are precipitated as insoluble carbonates as the water evaporates:

$Ca(HCO_3)_2 \xrightarrow{heat} CaCO_3 (s) + CO_2 (g) + H_2O (g) \dots (7.2)$

A similar reaction occurs if bicarbonates of magnesium are present in the water. Consequently, temporary hardness maybe removed simply by boiling. This process is responsible for the deposition of scale (insoluble carbonates) in boilers, water pipes and kettles during the heating of water.

A less common type of hardness in fresh waters is **PERMANENT HARDNESS**, due to the presence of calcium and magnesium sulfate and chlorides. These salts are not precipitated when water is boiled. Hard water can be softened by various methods, including the use of ion exchangers.



In practice Hardness can be measured by titration using indicator (EBT) and titrated against standard EDTA at pH 10.

As calcium and magnesium ions react with ethylenediamminetetraacetic acid (EDTA) to form strong complexes, their concentration in water can be determined by titrating a known volume of water with a standard EDTA solution using Eriochrome Black T (EBT) indicator to show the end point of the reaction.

At the start of the reaction, the EBT indicator forms complexes with the cation (Ca^{2+} and Mg^{2+}) and creates a red color (faint violate) solution. As DETA is added, this forms new complexes with Ca^{2+} and Mg^{2+} because the affinity between EDTA and the cations are bigger than that between EBT and the cations. When all the cations are linked to the EDTA, the indicator color change from red to blue. Consequently, the hardness of water can be calculated by measuring the amount of EDTA consumed by a water sample and relating this to the concentration of dissolved calcium and magnesium ions.

Time Required

Two hours, depending upon the number of water samples determined

Equipment:

- 1. 250 ml Erlenmeyer flasks
- 2. 100 ml volumetric cylinder
- 3. 50 ml burette
- 4. 10 ml measuring cylinder
- 5. Boss, clamp, retort stand and white tile
- 6. Tongs

Reagents:

Part A : Total Hardness

- 1. Ammonium hydroxide/ammonium chloride (NH₄OH/NH₄Cl) buffer at pH 10.
- 2. M ethylenediamminetetraacetic acid (EDTA)
- 3. Erochromic black T indicator
- 4. Suitable water samples (e.g. tap, lake or river waters)



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Part B : Calcium Hardness

- 1. 0.1 M sodium hydroxide (NaOH) buffer at pH 12-13.
- 2. 0.01 M ethylenediamminetetraacetic acid (EDTA)
- 3. Murexide indicator
- 4. Suitable water samples (e.g. tap, lake or river waters)

Significant Experimental Hazards

- Student should be aware of hazards associated with the use of all glassware (cuts), Bunsen burners (burns and fire) tongs to move hot objects (burns and dropping hazards) and fume cupboards.
- Hydrochloric acid is harmful by digestion and may cause severe burns to eye and skin.
- Eriochromic black T indicator may be harmful if ingested in quantity and may irritate eyes and skin. It may also stain clothing and skin.

Procedure:

Part A : Total Hardness

- 1. Measure 100 ml of water sample into a 250 ml Erlenmeyer flask.
- 2. Add 5-10 ml of NH₄OH/NH₄Cl buffer standard till you reach pH 10 and 3 drops of EBT indicator
- 3. Titrate the solution with standard EDTA until the indicator colour changes from red wine/ faint violet to pure blue.
- 4. Repeat this rough titration at least twice more, or until two concordant results are obtained.
- 5. Carry out the same determination by using other appropriate water samples.

Part B : Calcium Hardness

- (7) Measure 100 ml of water sample into a 250 ml Erlenmeyer flask.
- (8) Add 5-10 ml of NaOH buffer till pH 13 is reached and a add 0.1 0.2 g (tip of spatula) of Murexide indicator
- (9) Titrate the solution with standard EDTA until the indicator color changes from pink to purple color.
- (10) Repeat this rough titration at least twice more, or until two concordant results are obtained.
- (11) Carry out the same determination by using other appropriate waters.



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Calculation

$$TH (mg \ CaCO_3/l) = \frac{vol. of \ EDTA \times G \times 1000}{vol \ of \ sample}$$
$$Ca^{2+} (mg \ CaCO_3/l) = \frac{vol. of \ EDTA \times G \times 1000}{vol \ of \ sample}$$
$$Mg^{2+} (mg \ CaCO_3/l) = TH(mg \ CaCO_3/l) - Ca^{2+} (mg \ CaCO_3/l)$$

Where

G: mg CaCO₃ equivalent to 1.0 ml of EDTA titrant at the calcium indicator end point.

Magnesium concentration can be determined by the difference between the total hardness and calcium hardness.

Issues to consider for your practical report

- Are there alternative methods for determining the hardness of water? If so, how do they compare to this method?
- What is the source of the river and lake hardness?
- What are the typical water hardness values in river and lake water samples?
- What are typical water hardness values in rivers, streams, lakes and drinking water in Jordan/World?
- How can permanent hardness be removed for domestic and industrial purposes (mention at least 2 types and describe the processes)?
- What are the legal limits of hardness in drinking water?



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Exp	<u>eriment (9</u> Experin	<u>): Hardne</u> 1ental Re:	<u>ss of Water</u> sults	
Name			Date	
ID No.			Group	
Calcium Hardnes	SS			
EDTA (M)			Indicator	
Sample Volume of	Burette Re	ading	Volume of Col	or change
ID Sample (ml)	Initial	Final	EDTA (ml)	

(M)			Ir	ndicator	
Sample	Volume of	Burette Re	ading	Volume of	Color change
ID	Sample (ml)	Initial	Final	EDTA (ml)	



Sample ID Magnesium Hardness Image: Constraint of the second se	Magnesium Hardness						
	Sample ID	Magnesium Hardness					

Observations & Calculations:



[10] DISSOLVED OXYGEN (A)

or D.O., is the amount of oxygen

issolved Oxygen,

dissolved in a sample

of water. This is the oxygen which is free to react with chemicals or to be used by organisms in the water.

Dissolved oxygen concentrations in water are dependent on a variety of factors; Temperature, movement of water, Aeration, elevation (pressure) and aquatic life. The temperature determines the saturation point of oxygen in the water, with colder waters typically holding more oxygen. Water which is agitated by running through a stream or a trickling filter typically has a higher concentration of D.O. than does stagnant water since the agitated water has a greater surface area coming in contact with the air. Aerators also increase the surface area of air to water and increase the D.O. concentrations. Aquatic plants release oxygen into the water during the day when they perform photosynthesis.





On the other hand, D.O. is removed from water by a variety of natural reactions. In the wastewater treatment plant, microorganisms use up oxygen in the water just as we use up oxygen in the air. Fish and other aquatic organisms also use up oxygen. At night, plants take in oxygen rather than releasing it, further lowering the D.O.

levels. Finally, some compounds in the water react with, and use up, oxygen.

The D.O. content of water is very important in natural waters and in wastewater treatment plants because it determines which organisms are able to live in the water. Since wastewater treatment plants depend on bacteria to break down the organic compounds found in water, they must carefully monitor the D.O. content of the wastewater. If the amount of dissolved oxygen in the wastewater becomes too low, these bacteria will die and septic conditions will occur. Septic conditions can result in unpleasant odor and in fish kills.



A variety of methods can be used to test the D.O. content of water. This handout explains how to test D.O. using a D.O. meter and by titration. Since different brands



of D.O. meters are operated slightly differently, you should also refer to the manufacturer's instructions before performing this test.

D.O. meters are relatively accurate, and can usually obtain readings within 0.1 mg/L of the actual D.O. concentration of the water. However, this does not take into account interferences which can be caused by salts, sulfur-containing compounds, and chlorine. Nor does it consider improper readings which will result from air bubbles becoming dissolved in the sample water.



Time Required

Two hours, depending upon the number of water samples determined

Equipment:

• DO prob.

Reagents:

• Suitable water samples (e.g. samples of settled sewage and final effluent from a local water treatment plant)

Significant experimental hazards

• Student should be aware of hazards associated with the use of all glassware (cuts), electrical equipment (shock, burns) and fume cupboards.

Procedure:

- (1) Wash the D.O electrode with distilled water before using it.
- (2) Immures the electrode in the beakers containing Liquid samples in the laboratory, write the condition of each beakers and the measured D.O with the units plus the temperature of each solution.
- (3) Wash the electrode before using it for the other sample and repeat the procedure that was carried out earlier.



Issues to consider for your practical report

- What are the potential sources of error in this analytical determination? How could they be overcome?
- What are alternative methods for determining the DO of aqueous samples? How do they compare to this method?
- What are typical DO values of water in Jordan? How do your data compare with these values?
- What are the main sources of DO in water and wastewater?
- What are the potential health and environmental effects if any of extreme DO values
- Compare between the values of DO obtained during the lab and the condition of each sample.







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	<u>Experiment (10): Dissolved Oxygen (A)</u> Experimental Results					
Name	Date					
ID No.	Group					

Sample ID	DO (mg/l)	Temperature °C	Salinity mg/l	рН	Observations



Observations & Calculations:





[11] DISSOLVED OXYGEN (B)

Dissolved oxygen (DO) levels in environmental water depend on the physiochemical and biochemical activities in water body and it is an important useful in pollution and waste treatment process control. Two methods are commonly used to determine DO concentration: (1) The iodometric method which is a titration-based method and depends on oxidizing property of DO and (2) The membrane electrode procedure, which works based on the rate of diffusion of molecular oxygen across a membrane.

In the Iodometric method, divalent manganese solution is added to the solution, followed by addition of strong alkali in a glass-stopper bottle. DO rapidly oxidize an equivalent amount of the dispersed divalent manganese hydroxide precipitates to hydroxides of higher valence states.

In the presence of iodide ions in an acidic solution, the oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent of the original DO content. The iodine is then titrated with a stranded solution of thiosulfate. The titration end point can be detected visually with a starch indicator. Some oxidizing and reducing agents present in solution can interfere with the iodometric method. Oxidizing agents liberate iodine from iodides (positive interference) and some reducing agents reduce iodine to iodide (negative interference). Also, organic matter present in solution can be oxidized partially in the presence of oxidized manganese precipitate, thus causing negative errors. Thus some modification of procedure is required.

The Winkler's method is a means of measuring the dissolved oxygen in a water sample by using a redox titration. In this method a white precipitate of manganese (II) hydroxide is produced by the action of sodium hydroxide on manganese (II) sulfate and the dissolved oxygen converts this into an orange-brown precipitate of manganese (IV) hydroxide:

$Mn^{2+} (aq) + 2OH^{-}(aq) \rightleftharpoons Mn(OH)_{2}(s)$ (1)	Manganese (II) hydroxide
$Mn(OH)_2(s)+1/2 O_2(aq) \rightleftharpoons MnO(OH)_2(s)$	Manganese (IV) hydroxide (2)



When potassium iodide is present in the solution, the manganese (IV) hydroxide librates iodine upon addition of an acid (H2SO4) in an amount equivalent to the quantity of dissolved oxygen originally present:

$MnO(OH)_2(s)+2I-(aq)+4H^+(aq) \rightleftharpoons Mn^{2+}(aq)+I_2(g)+3H_2O(l)$

Measurement of the amount of iodine allows the concentration of dissolved oxygen to be determined. Sodium thiosulfate converts the iodine back into iodide ions and this reaction can be monitored volumetrically:

$I_2(g) + 2S_2O_3^{2-}(aq) \rightleftharpoons S_4IO_6^{2-}(aq) + 2I^-(aq)$

With the presence of Starch, as an indicator, the color of the sample turns from yellow to Blue. When the sample is titrated against sodium thiosulfate, the color changes from blue to Colorless, which is the end point.

Time Required

Two session of two hours duration, separated by a period of either five or seven days, depending upon weather you decide to determine BOD_5 or BOD_7 and upon the number of samples determined (assuming all reagents are made up in advance.

Equipment:

- 1. Winkler's Bottles (300 ml)
- 2. Incubator thermostatically controlled at $20^{\circ}C \pm 1^{\circ}C$ from which all light should be excluded to prevent formation of dissolved oxygen by algae in the sample
- 3. 250 ml conical flasks
- 4. 2 ml pipettes and pipette filler
- 5. 100 ml burette
- 6. 10 ml measuring cylinder
- 7. Boss, clamp, retort stand and white tile

Reagents:

- 1. Sodium Thiosulfate Solution (Na₂S₂O₃)
- 2. Manganese Sulfate Solution
- 3. Alkaline iodide-azide solution. (sodium hydroxide (NaOH) and sodium iodide (NaI) and sodium azide (NaN₃)
- 4. Starch indicator
- 5. Concentrated sulfuric acid (H_2SO_4)
- 6. Suitable water samples (e.g. samples of settled sewage and final effluent from a local water treatment plant)





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Significant experimental hazards

- Student should be aware of hazards associated with the use of all glassware (cuts), electrical equipment (shock, burns) and fume cupboards.
- Sulfuric acid is harmful by ingestion and may cause severe burns to eyes and skin.
- Sodium thiosulfate maybe harmful if ingested in quantity and may irritate eyes and skin
- Alkaline iodide-azide solution causes severe burns and may be harmful if ingested.
- Manganese sulfate solution is be harmful by ingestion and may irritate eyes and skin.

Procedure:

- (1) Place the incubation bottle in fume cupboard on a layer of disposable absorbent paper.
- (2) Using a pipette for each addition, add 1.0 ml of manganese sulfate solution and 1.0 ml of alkaline iodide-azide solution. *In each case, ensure that the tip* of the pipette is well below the surface of the liquid in the bottle.
- (3) Incline the bottle and carefully replace the stopper so as to avoid the inclusion of air bubbles. Some of the water sample will spill out of the bottle as you replace the stopper; ensure that your hands do not come into direct contact with the liquid and dry the outside of the bottle with a disposable paper towel.
- (4) Thoroughly mix the contents of the bottle by inverting the bottle at least 20 times and then allow the precipitate to settle.
- (5) Repeat the mixing and allow the precipitate to settle again to leave a completely clear supernatant liquid.
- (6) In a fume cupboard, add 1.0 ml of concentrated sulfuric acid very slowly and carefully down the neck of the bottle. (Take all sensible precautions when performing this procedure, including lowering the sash of the fume cupboard and wearing protective glasses and gloves.)
- (7) Replace the stopper in the bottle and mix its contents thoroughly by inversion until all of the precipitate has dissolved. If the precipitate does not dissolve instantously, allow the bottle to stand for a few minutes and repeat the mixing procedure. In either case, mix the contents of the bottle again immediately before measurement.
- (8) Accurately transfer 200 ml of the solution to a 250 ml conical flask and immediately titrate the iodine present with standard sodium thiosulfate solution. When the brown color, due to iodine, has changed to a pale straw color, add starch indicator to produce a blue coloration. The titration is then continued until the blue color just disappears.
- (9) Repeat the same procedure for all samples.







Calculation

From the previous equations, it can be seen that 2 moles of thiosulfate are equivalent to 0.5 mole of dissolved oxygen.

The concentration of the thiosulfate solution is 0.0125 M and therefore 1 ml of this solution contains 0.0125*10-3 moles. Thus:

1 ml of 0.0125 M thiosulfate solution = $\frac{1}{4}$ (0.0125*10-3) moles DO

1 ml of 0.0125 M thiosulfate solution = $\frac{1}{4}$ (0.0125*10-3)*32 g DO

1 ml of 0.0125 M thiosulfate solution = 0.1 mg DO

Dissolved Oxygen, $mg/l = \frac{Volume \ of \ thiosulphate \times M \times 1000}{Volume \ of \ sample}$

Issues to consider for your practical report

- What are the potential sources of error in this analytical determination? how could they be overcome?
- Are there alternative methods and indicators available for measuring the DO content of water samples? If so, how do they compare to this method?
- What are the legal limits of DO in natural and drinking waters? Do your values exceed such legal limits?
- What are the potential human health and environmental effects (if any) of less DO in potable and natural waters?