CHEMISTRY EXTENDED ESSAY

Investigation of, Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) effects on water hardness and taste by using EDTA (Ethylenediaminetetraacetic Acid) Method and clarification between pH and total hardness.

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1. ABSTRACT

A question "what causes the taste difference between the water I drink?" came to my mind during the planning stage of this test? I had four different water to figure out this. I thought about reasons for the difference between this water, what kind of metal-based softening was made when softening water hardness, factors they were dependent on and how they changed or did not change. I wanted to investigate what was the water hardness of the samples used and to which hardness standard these samples conform by using the EDTA (Ethylene Diamine Tetra Acetic Acid) method and by determining the calcium and magnesium amounts and total hardness ratios. In addition, I decided to investigate reflection of these metal ions on pH.

Water is the most important compound which is necessary for the existence and survival of mankind. About 4/3, in other words, 80%, of our world consists of water and only 1% of this water is drinkable. Water is the most abundant compound in living being. 80% of children's weight and up to 55-60% of adults' weight consists of water.[1] However, the ratio of potable water is becoming increasingly inadequate depending on the increasing rate of population growth and seasonal changes. Therefore, it is necessary that water should become potable. This condition of becoming potable is generally achieved by dilution or softening using various methods and by reducing and even eliminating of various elements (calcium, magnesium, iron) in water. Thus, water becomes potable both in terms of taste and appearance. Recycling of water, our most basic need, is achieved in this way.

Water hardness is defined as the feature of water to consume soap (without foaming). Water from natural resources absorbs CO_2 from the air and thus, becomes acidic. Such water releases salt inside of rocks consisting of Mg^{+2} and Ca^{+2} when it comes into contact with them. Water containing such Mg^{+2} and Ca^{+2} salts at certain rates is referred to as hard water.

If soaps with sodium and potassium content are added into such water, Na^{+} and K^{+1} ions are replaced by Mg^{2+} and Ca^{2+} ions and cause the formation of precipitates. This situation continues until precipitation of all the ions causing hardness. Soap will begin foaming after all of Mg^{2+} and Ca^{2+} ions in the setting precipitated. [2]

The process of transforming and precipitating Ca^{2+} and Mg^{2+} metals into water soluble and non-water soluble compounds when performing processes for water hardness or the process of replacement of Ca^{2+} and Mg^{2+} elements with sodium element as with zeolite is referred to as softening of hard water.

Thus, the efforts performed have revealed whether the differences between the two water are caused by Mg^{2+} or Ca^{+2} and it has been endeavoured to facilitate understanding of the process with the methods applied.

2. INTRODUCTION

A water molecule consists of two hydrogen atoms and one oxygen atom. An acid containing H^+ atoms results from reaction of a base containing OH^-. Melting point and freezing point of water is 0°C and 100°C, respectively. While there is a covalent bond between its molecules (H_2O) hydrogen and oxygen atoms, the chemical bond between H^+ and O^{-2} of water molecules is a hydrogen bond (Figure 1). Hydrogen bond is a covalent bond that is made by 7A elements with a high electronegativity. Electrons are attracted by atoms with high electronegativity. Thus, the hydrogen ion remaining without electron attracts non-shared electron pair and creates a hydrogen bridge. Water is a polar molecule (Figure 2). While the oxygen atom inside water carries (-) pole load, the hydrogen atom carries (+) pole load. It serves as a very good solvent against a variety of aldehydes, ketones and hydroxyl-acid with this polarity.

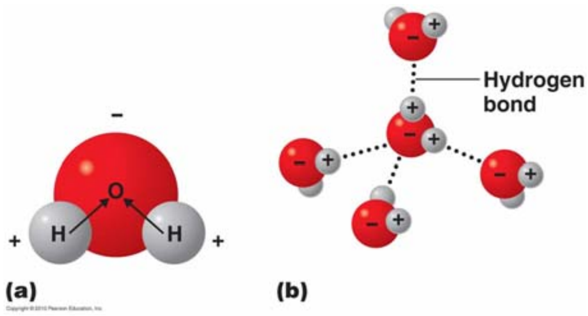

Figure 1: Hydrogen bonds between oxygen and hydrogen in a water molecule

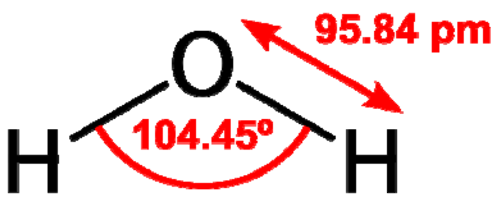

Figure 2: The angle between hydrogen and oxygen atoms.

In addition to all these features, calcium, magnesium, carbonate and bicarbonate ions available in natural water are also of great importance for living creatures.

Calcium and magnesium elements are 2A group elements and referred to as alkaline-earth metals. Atomic numbers of calcium and magnesium are 20 and 12, respectively.

Ca^{2+} ions are an essential nutrient for plants and algae. They are necessary for reducing of water permeability of cell membranes in aquatic animals and maintaining their structural and functional integrity.

Mg^{2+} ions increase productivity in aquatic environment. As it is contained also in chlorophyll, it is a necessary cation for plants. It may be harmful depending on the anions it compounds.

Bicarbonate pump is very important for human blood, because it ensures pH adjustment by making very important arrangements existing in the blood. [2]

Hardness of water is due to its ability to dissolve. Some water has more ability to dissolve, in other words, the ability to soften, depending on dissolved materials in its content. For example, they dissolve carbon dioxide, limestone and magnesium in water easier and cause these materials transform into bicarbonates. Carbon dioxide ratio of water in contact with plants is quite high.

Hardness of groundwater is higher than the hardness of surface water because groundwater is in more contact with underground mineral substances. This is why it is also referred to as mineral water. The cause of hardness of natural water is the contact of such water with soil and rock formations. As dissolved gas content in water increases, water pH constantly reduces. pH of rainwater reduces because it can contain dissolved atmospheric gases. It also dissolves some ingredients in soil and rocks when it falls on the ground.[3]

However, rainwater with an approximate pH value of 7 does not suffice dissolve and carry all the ingredients causing hardness that are available in large amounts in natural water. When rainwater fall on the ground in this way, it cannot dissolve all the ingredients causing hardness. It ensures CO_2 gas occurring as a result of bacterial activities of acidic conditions in the soil to dissolve in order to ensure these ions to pass through the soil.

Elimination of ions dissolved in water is referred to as reducing of water hardness. Thus, tap water becomes potable. The basic principle of water treatment machines is to eliminate calcium, magnesium and materials from water and thus, ensure water to soften. Water hardness refers to the bitter taste of water occurring due to salts and metals available in it. This hardness should be eliminated and water should become potable. Hard water damages human health and leads to environmental pollution by increasing the consumption of soaps. Therefore, various methods are applied in order to reduce the hardness. Water hardness is divided into two, being as permanent and temporary hardness, depending on the nature of salts causing hardness. Hardness is all about with cations, such as calcium and magnesium, available in water. Hardness has nothing to do with anions.[4]

1. **Temporary hardness:** Temporary hardness refers to the hardness caused by Ca and Mg bicarbonates. Such hardness can be eliminated by boiling water for a certain time period. Hardness will have been eliminated after boiling. Bicarbonate salts transforms into poorly water-soluble carbonate salts and thus, poorly water soluble and thus, precipitate.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2$$

2. **Permanent hardness:** Permanent hardness refers to the hardness caused by $CaCl_2$ and $MgCl_2$, SO_4^{-2}, PO_4^{-3} or silicate salts. Such hardness cannot be eliminated by boiling.

The sum of permanent and temporary hardness is referred to as overall hardness.

Various definitions are used to define as hardness. These include;

German Hardness: It refers to the amount of calcium ions equivalent to 1 mg of CaO in 100 ml of water.

French Hardness: It refers to the amount of calcium ions equivalent to 1 mg of $CaCO_3$ in 100 ml of water.

British Hardness: It refers to the amount of calcium ions equivalent to 1mg of $CaCO_3$ in 70 ml of water.

1 German Hardness = 1.25 British hardness = 1.79 French hardness

Classification of water based on hardness degrees:

Degree	**German hardness**	**French hardness** [4]
Very Soft	0-4	0-7.2
Soft	4-8	7.2-14.5
Average Soft	8-12	14.5-21.5
Hard	12-18	21.5-32.5
Very Hard	18-30	31.5-54.0

3. BACKGROUND INFORMATION

There are several methods to determine and eliminate water hardness.

3.1. Lime-Soda Method: The lime-soda method is also referred to as chemical precipitation method. The purpose here is to render molten ingredients in water non-meltable and non-precipitateable.[5]

Lime ($Ca(OH)_2$) and soda (Na_2CO_3) amounts required to soften water samples are calculated using experimental methods, in other words, based on coefficients of reactions given by lime and soda with Ca^{2+} and Mg^{2+} ions. While lime is used to eliminate carbonate hardness and temporary hardness, soda is used to eliminate permanent hardness.

This process works as follows; water sample with a higher ratio of water hardness than the ratio it should be is treated first with lime and then soda. While lime is added into water in the form of Ca $(OH)_2$, soda is added in the form of Na_2CO_3. At this stage, water hardness is precipitated in the form of calcium carbonate and magnesium hydroxide. The necessary condition to precipitate this magnesium hydroxide depends on its pH value. The pH value must be greater than 9 for magnesium hydroxide to precipitate. ($pH>9$). To achieve a much better precipitation, a very small amounts of aluminium and sodium aluminate can be added.

The lime-soda method is implemented in two different forms in practice, being as cold lime-soda method and hot lime-soda method. While the cold lime-soda method is used to soften city, cooling and factory water, the hot lime-soda method is used to soften feed water of steam boilers. Since the process is carried out at a temperature close to the evaporation temperature of water in the hot lime-soda method, coagulation and sedimentation takes place easily.

CO_2 that is in free-state contained in lime is released and coagulates molten ingredients in the compound.

Elimination of carbon dioxide;

$CO_2 + Ca(OH)_2 \rightarrow CaCO_3(s) + H_2O$

Elimination of calcium bicarbonate;

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3(s) + H_2O$

Elimination of magnesium bicarbonate;

$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 (s) + CaCO_3 + 2H_2O$

$MgCO_3 + Ca(OH)_2 \rightarrow CaCO_3 + Mg(OH)_2 (s)$

Elimination of calcium sulphate;

$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3(s) + Na_2SO_4$

Elimination of magnesium sulphate;

$Mg SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Mg(OH)_2 (s)$

3.2. Ethylene Diamine Tetra Ethyl Acetate (EDTA):

Ethylene Diamine Tetra Ethyl Acetate (EDTA) or its sodium salt is used as titration solution. These compounds are generally referred to as EDTA and give complexes causing Ca^{+2}, Mg^{+2} and other divalent hardness. Thus, calcium and magnesium amounts are also determined by this method.

M-EDTA complex → occurs as a result of M^{2+} + EDTA [M-EDTA] reaction.

(M: Mg or Ca)

The overall hardness can be determined as follows by using the EDTA titration: A sample of 25 ml is diluted about 50 ml using distilled water in an erlenmeyer. Then, a buffer solution of 1 ml and 1 to 2 drops of indicator solution are added. The EDTA solution is titrated until a clear colour change is observed.

3.3. Cation-Anion Exchange Method:

The method that is most widely used to soften water hardness is ion exchange resin method. The chemical structure of ion exchange resins consists of polymerized hydrocarbons containing non-ionizing or ionisable groups and highly available in the network structure. Resins may also be used at temperatures above 100°C because they are highly stable. These resins are also resistance to acids and bases in concentrated amounts and too many oxidizing and reducing agents. Ionic group constituting the resin base determines properties of the ion exchanger. When basic functional groups are attached to resins, anion exchangers would have formed. It refers to loading of resin with positive load. Chemical stability of anion exchangers is lower than cation exchangers. Amines are hydrogenated instantly at high temperatures and this reduces capacity, in other words, stability of ion exchangers. It causes the solution to evaporate together with soluble organic substances:

- Ion exchangers contain large amount of polar groups, and resins have a strong hydrophilic structure and attract water. They swell, shrink and act like a hygroscopic gel. 1 gram of dry resin absorbs 0.5 to 1 gram of water.
- Ion exchange resins with a light porous solid structure are prepared on materials such as sphere, bead or plate. (Figure 3)

They are used for the process of elimination of Ca^{2+} Mg^{2+}, Fe^{2+} and Mn^{2+} ions in water (water softening) in the industry. Anions remaining behind in water with cation exchanged are also subjected to anion exchangers. For this purpose, melamine-type plastics can be used by using OH^- groups. NaOH solutions are used to regenerate anion exchangers. Oxygen available in dissolved state in water also causes corrosion. In order to eliminate this, an appropriate amount of Na_2SO_3 or hydrazine is added to water. [6]

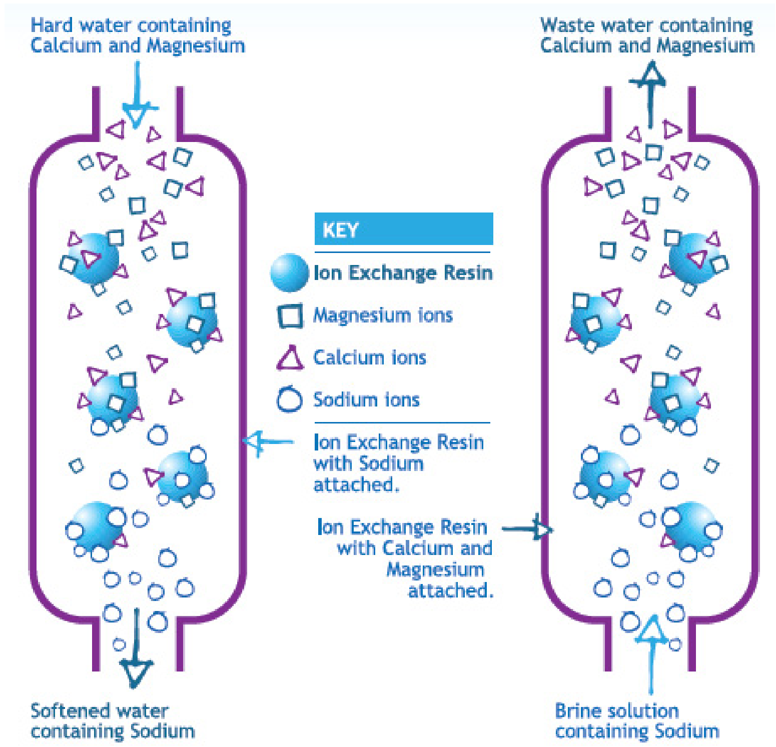

Figure 3: The usage of ion exchanging resin

3.4. Aluminium Sulphate and Alum Method:

Aluminium sulphate can be hydrolysed both directly ($Al_2(SO4)_3.18H_2O$) and in water ($Al_2(SO_4)_3$).

$Al (SO4)_3 + 6H_2O \rightarrow 2Al (OH)_3 + 3H_2 SO_4$

Affects the resulting H_2SO_4 bicarbonate and

Causes the reactions of $Ca (HCO_3)_2 + H_2SO_4 \rightarrow CaSO_4 + 2CO_2 + 2H_2O$

$Mg (HCO_3)_2 + H_2SO_4 \rightarrow MgSO_4 + 2CO_2 + 2H_2O$

and thus, temporary hardness is eliminated.

Another benefit of this method is that $Al (OH)_3$ created by aluminium sulphate hydrolysed in water precipitates substances casing turbidity in water. Only CO_2 remains in water. CO_2 remaining in water is eliminated by the method of passing through heating or gas absorber equipment.

3.5. Phosphate Method:

It is a method used from old times. The high prices of phosphate have delayed implementation of this method, but using this method has become necessary due to the increased use of high-pressure boilers in technical field overtime.

Before eliminating hardness using the phosphate method, other methods are applied first and then, this method is used only there is any hardness remaining, because temporary hardness should be eliminated in advance by other methods in order to achieve a good result with the phosphate method. Eliminating the remaining hardness by this method is more cost-effective.

Therefore, this method is applied in conjunction with other methods.

Some of the reactions released during the implementation of the phosphate method include:

$$3Ca(HCO_3)_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6NaHCO_3$$

$$3Mg(HCO_3)_2 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2 + 6NaHCO_3$$

$$3Ca(SO_4) + 2Na_3 PO4 \rightarrow Ca_3(PO_4)_2 + 3Na_2SO_4$$

$$3MgCl_2 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2 + 6NaCl$$

3.6. Permutite (Zeolite) Method:

This method consists of the reaction causing the change of Ca^{2+} ve Mg^{2+} ions with alkaline earth metal ions (Na^+) on silicate surfaces of certain hydrogenated alkali earth metals, called zeolite. After this process, time or flow-controlled regeneration process of the saturated resin should be performed with salt water.

Zeolite-operated tools become non-functional at the end of Na^+ cation after a certain period of time. In this case, a concentrated NaCl solution is sent on the used zeolite in order to freshen (to regenerate) the zeolite. Ion exchange capacity of natural zeolites is very little. These are harsh and less porous substances. They are less sensitive to foreign substances.

Permutites are more porous than those of the natural and have a larger surface area. Consequently, they are susceptible of foreign organic substances. 1 m3 of zeolite extracts 3600 to 3900 of CaO from water instantly at the time of filtration. However, the same amount of synthetic zeolite (neo permutite, invertit, vebolit etc.) extracts 11000 to 15000 of CaO from water. Synthetic zeolites are preferred for water with relatively less iron content and normal pH level. Natural zeolites are used for water with less hardness, high iron content and high or low pH value. Another disadvantage of permutite is its susceptibility of foreign matters since it is highly porous. Their large surfaces facilitate them to exchange substances.

4. METHOD

Out of these six processes EDTA method is chosen in order to understand more clearly the degree of effect of calcium and magnesium in hardness. Underlying the study question, the standards that the selected water meets and the correlation with pH and to make comparative comments. The EDTA method ensures the understanding of reagents that are used more commonly and values of calcium and magnesium available in water and the effect of these values on the total hardness of water. Reagents are quite readily available and affordable. This experiment has additionally provided us with the opportunity to understand and interpret the relevant standards of the samples used and the hardness degree of the water.

4.1. EDTA (Ethylene Diamine Tetra Acetic Acid)

The EDTA (Ethylene Diamine Tetra Acetic Acid) method allows for determining calcium, magnesium and total hardness ratios of water and investigating standards which the hardness of water conforms to and level of the softness of water. In order to prove the accuracy of the given data, an EDTA and ammonia/ammonium chloride buffer solution was used to calculate the hardness of water. The effect of hardness on the taste of water has been studied comparatively. EDTA or its sodium salt is used as titration solution. These compounds are generally referred to as EDTA and give complexes causing Ca^{+2}, Mg^{+2} and other divalent hardness. Thus, calcium and magnesium amounts are also determined by this method. [7]

4.1.1. Materials used in the EDTA Method

- Magnetic Stirrer
- Automatic Burette (0,1 division)
- Erlenmeyer
- Volumetric flask
- Distilled water

4.1.2. Chemicals used in the EDTA Method

- 0,02 N EDTA (Ethylenediaminetetraacetic acid) : 3,72g/1000ml
- Ammonia Ammonium Chloride Buffer Solution:
- The solution is completed with distilled water up to the volume of 6.92 g of Ammonium Chloride + 57 ml of Concentrated Ammonia + 100 ml
- Eriochorome Black T: 1 g of Eriochorome Black T and 10 g of NaCl is pounded and mixed thoroughly in a mortar.

4.1.3. Experimental

- **EDTA solution, 0.01 M:** Approximately 3.75 g of EDTA is weighed. To keep pH value of the solution as 10.5, the solution is dissolved using 17 mL 1 M NaOH and completed with distilled water to 1 L in a volumetric flask.
- **Standard solution to set EDTA:** 0.2 g of pure $CaCO_3$ is weighed and put in a capsule.
- It is acidified 3 times with distilled HCl, evaporated, washed with distilled water and completed to 1 L. This is a standard solution at a hardness of 20 oF.
- **NH_4OH + NH_4Cl buffer solution (for total hardness):** 65 g of NH_4Cl (ammonium chloride) is dissolved in 400 ml of ammonia and completed to one litre with distilled water.
- **1 M NaOH solution (for Ca^{2+} hardness):** 40-50 g of NaOH solution is dissolved in water and completed to one litre with distilled water.
- **Eriochrame Black T. Indicator (for total hardness):** 0.2 g of Eriochrame Black T. is powdered in a mortar with 80 g of NaCl and kept in a dark-coloured bottle.
- **Murexide-indicator (for Ca^{+2} hardness):** 0.2 g of murexide is powdered in a mortar with 100 g of NaCl and kept in a dark-coloured bottle.
- **Setting 0.01 M EDTA:** 3 solutions of 100 ml is taken from the standard hard water into the erlenmeyer, and approximate consumptions of the solutions are calculated by applying the Ca hardness determination method.
- **Total Hardness:** 100 ml of water sample is taken (the amount required to keep 0.5 to 2.0 mL pH at 10), buffer solution (NH_4Cl+NH_4OH) is added and 0.01 M of EDTA (Tritriplex III) is added until the colour turns from wine red into blue after adding 0.1 g of the total hardness indicator (Eriochrame Black T+NaCl).

- **Calcium Hardness:** 100 ml of water sample is taken and 2-4 mL of 1 M NaOH solution is added. [In order to precipitate Mg^{2+} in hydroxide form and keep pH value of the setting at around 11, the solution is titrated with 0.01 M of EDTA until the colour turns from pink into violet after adding 0.1 g of murexide indicator (it colours only with Ca^{2+} ions)].

4.1.4. Calculation

Total Hardness;

Consumption = oF Hardness (Total Hardness), or Consumption x 10 = Total Hardness (mg/L CaCO3)

Calcium Hardness;

Consumption x 10 = Ca^{+2} Hardness (mg/L) in $CaCO_3$; = Consumption = oF Hardness.

If desired;

[Total Hardness - Ca^{2+} Hardness = Mg^{2+} Hardness]

Calculation of Calcium Amount;

(mg/L)Ca = (A x N x2000)/Sample volume (Ml)

A = ml of the EDTA solution consumed for Calcium Hardness

N = Normality of the EDTA solution

Calculation of Magnesium Amount;

(mg/L) Mg= (A x N x1200O)/ Sample volume (Ml)

EDTA solution (mL) consumed for Total Hardness - EDTA solution (ml) consumed for Calcium Hardness = ml of the EDTA solution consumed for magnesium

N= Normality of the EDTA solution[8]

5. RESULTS

	Sample 1	Sample 2	Sample 3	Sample 4
Calcium	**25.70 mg/L**	**37.54 mg/L**	**78 mg/L**	**32.22 mg/L**
Magnesium	**9.73 mg/L**	**1.72 mg/L**	**24 mg/L**	**4.24 mg/L**
pH	7.60	7.96	7.2	8.22

6. Data Collecting, Analysis

ANALYSIS RESULTS

	Sample 1	Sample 2	Sample 3	Sample 4
Total Hardness	2 mg/L 100mg/$CaCO_3$ L	3333mg/L 6667mg/$CaCO_3$ L	5.9mg/L 295mg /$CaCO_3$ L	3333 mg/L 6667mg/$CaCO_3$ L
False Hardness	1059mg/L 32553mg/ $CaCO_3$ L	0.2mg/L 95652mg/ $CaCO_3$ L	8852mg/ L 94426mg/ $CaCO_3$ L	7826 mg/L 73913mg/ $CaCO_3$ L
Permanent Hardness	3mg/L 150mg/ $CaCO_3$ L	0.2mg/L 33333mg/ $CaCO_3$ L	0.2mg/L 32788 mg/ $CaCO_3$ L	6448 mg/L 73224mg/ $CaCO_3$ L

Temporary Hardness	5mg/L 250mg/ $CaCO_3$ L	2mg/L 100mg/ $CaCO_3$ L	9344mg/ L 9672mg/ $CaCO_3$ L	8689mg/L 3443mg/ $CaCO_3$ L

7. CONCLUSION - DISCUSSION

As a result of the diluting and softening the four different brands of water I have used for my experiment with the EDTA method, determination of the total hardness and conclusion of to which hardness standard they meet and whether or not their hardness are ideal or whether or not they should be softened has been found. Comparison of the calcium and magnesium amounts are written with the data.

According to data I have obtained as a result of the experiment at the end of EDTA experiment, hardness of the samples 1, 2 and 4 has average hardness and is not needed to be softened. However, although hardness level of the sample three is quite high, its hardness should be softened, in other words, its calcium and magnesium contents should be reduced.

When calcium (Ca^{+2}) and magnesium (Mg^{+2}) amounts are compared, calcium content of the samples from the highest to the lowest is sample three, sample two, sample four and sample one respectively. When the magnesium amounts are compared, calcium content of the sample three is higher than the sample one and of the sample one than the sample four. Consequently, it is seen that calcium has an effect on hardness of the water higher than magnesium.

If it is desired to establish a correlation between the pH values and the hardness, it is seen that the sample four is more alkali compared to the sample three. We see that hardness of the water reduces as the level of alkalinity of the water increases and thus, they become more potable.

Also if were to observe the tastes of the samples, the third sample has an distinctive taste difference which was more like sour and also sample two is somewhat sour. So more the hardness sourer the taste. Finally the samples two and four had bland usual water taste because their softness.

We have had the opportunity to clearly observe the results with data that we aimed to reach at the end of this experiment.

8. EVALUATION

8.1. RANDOM ERROR

EDTA and other substances we used may have some preparation errors, such as their concentration. In this case, the amounts were considered equal and or within the acceptable error limit for all samples. Errors occurred during weighing of the catalysts and measuring of the NaOH and Eriochrome Black T. indicator are within the acceptable error limit, but should not be ignored.

8.2. Systematic Error

The purity of EDTA we used as the experiment catalyst was not 100%. It may differed but the purity level is within the acceptable error limit since the ratio for purity level of the EDTA is the same for all the samples.

Bibliography (Both Turkish and English Publications)

1. Principles of Biochemistry, 1993, A.L. Lehninger, D.L. Nelson and M.M. Cox.,Worth Pub.Inc.N.Y.

2. Kantitatif Analiz Laboratuvar Kitabı, 1984, T. Gündüz, Ankara University. Fen Fak. Publications, Ankara.

4.Çelik, J., ‘ Türkiye Içme Su Limiti Ne Olmalıdır’

3. Boysan, F., Sengörür, B., 2009. “Su Sertliginin insan Sağlığıı için Önemi”, SAU Fen Bilimleri Dergisi, 13. Cilt, 1. Sayı, s. 7-10.

5. Yıldız Technical University Çevre Mühendisligi Bölümü, “Sertlik Tayini” Çevre Kimyası Lab. Report.

6. Yıldız Technical University Çevre Mühendisligi Bölümü, kimyasal temel işlemler Lab. Report

7. http://web.hitit.edu.tr/dersnotlari/ibrahimbilici

8. Analitik ve Sınai Kimya Laboratuvarı, 1984, M. Demir, Ş. Demirci ve A. Usanmaz, M.E.B Publications.

9. Sivas Cumhuriyet Üniversitesi Çevre Mühendisligi Bölümü, “Kalsiyum Magnezyum ve Sertlik Tayini” Çevre Kimyası Lab. Report.