DETERMINATION OF TOTAL HARDNESS (CaCO3) AND (MgCO3) OF WELL WATER IN SAMPUABALO VILLAGE BY COMPLEXOMETRY TITRATION METHOD

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ARTICLE INFORMATION

Received: 4 April 2025
Revised : 9 Mei 2025
Accepted: 25 Juni 2025
DOI:

KEYWORDS

Keywords: well water, hardness, complexometric titration.

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A B S T R A C T

Water has a very important role for humans in meeting daily needs, such as drinking, cooking, washing, transportation, agriculture, and industry. One of the properties of water that needs to be considered is disparity, which is a characteristic of water caused by the presence of divalent metal ions, such as calcium (Ca^{2+}) and magnesium (Mg^{2+}), which can react with soap and produce crust. In this study, the complexity titration method was used because it has an advantage in the quantitative analysis of metal ion levels in water samples. This method has high selectivity for metal ions, easy implementation, and good accuracy in measuring the total hardness of water. With the right indicators, the color change at the equivalent point can be clearly observed, thus providing reliable results in determining water hardness. This study aims to determine the total hardness of well water in Sampuanbalo Village using the complexity titration method. Samples were taken from three wells located in lowlands, temperate plains, and highlands. The results of the analysis showed that the total hardness level in the form of $CaCO_3$ in the samples of wells in the lowlands was 312 mg/L, 286 mg/L, and 332 mg/L. Meanwhile, in the wells in the lowlands, the modified $CaCO_3$ levels were 286 mg/L, the medium plains were modified 180 mg/L, and the highland was modified 266 mg/L. Meanwhile, The total hardness level in the form of $MgCO_3$ in lowland wells was 262.08 mg/L, medium plains 240.24 mg/L, and highlands 278.88 mg/L. In lowland wells modified $MgCO_3$ levels were 240.24 mg/L, medium plains modified 156.34 mg/L, and plateau modified 223.44 mg/L. Although cooked water showed a decrease in soberness levels, However, the nature of the hard water is still included in the category of hard water.

INTRODUCTION

Water has an important role in human life, meeting various daily needs such as drinking, cooking, washing, transportation, agriculture, and industry (Sari et al., 2019). The hardness level of groundwater (well water) varies in different locations, and in general, well water tends to have a higher level of hardness. This is due to direct contact between water and limestone layers in the soil where the well is located (Nyoman, Amri, & Harun, 2018).

Groundwater (well water) has several disadvantages compared to other water sources, as it contains high concentrations of mineral compounds, such as magnesium (Mg^{2+}), calcium (Ca^{2+}), and iron (Fe^{2+}), which can cause water hardness (Munfiah et al., 2013). Factors that can reduce water quality include seasonal changes, well construction conditions, soil type and slope, distance from pollution sources, and the activities of living things around the well (Nugroho, 2013).

Hardness in the water can cause the water to become cloudy and interfere with the saponification process, because the mineral ions Ca^{2+} and Mg^{2+} react with the anions from soap (Megawati et al., 2013). Based on the severity level, water can be categorized as follows: <50 mg/L (classified as soft water), 50-150 mg/L (classified as medium water), 150-300 mg/L (classified as hard water), and >300 mg/L (classified as very hard water) (Musiam & Darmani, 2015). Various methods have been widely applied to reduce the levels of metal ions Ca^{2+} and Mg^{2+} that cause water hardness, such as precipitation using chemicals, ion exchange resins, and adsorption (Atastina et al., 2008). There are several ways to measure the level of water hardness, including acid-base titration, precipitation titration, reduction-oxidation titration, and complexometry titration (Melati et al., 2022).

Complexometry titration is a type of titration in which titrants, such as NaEDTA, form complexes with metal ions on the titration. The basic principle of complexity titration is the formation of complexes between metal ions, such as Ca^{2+} ions, and EDTA, so that the levels of metal ions in solution can be known (Saputri & Nofita, 2018). This method is based on the formation of complex ions in a solution, where the complex between the metal and EDTA has high stability. The addition of the NRE indicator to a solution containing calcium and magnesium will result in a burgundy color, which helps to identify the titration endpoint easily. In addition to the NRE indicator, a pH 10 buffer solution is also added to maintain the alkaline condition of the solution during titration (Astuti, 2016).

EDTA (Ethylene diamine tetraacetate) is used as a complicating agent in the analysis of calcium containing phosphate by atomic absorption spectrophotometry (Natalia et al., 2021). EDTA serves to bind Ca and Mg ions, forming a stable complex. The titration endpoint is reached when all Ca and Mg ions have been bound by EDTA, which is characterized by a change in the color of the solution from burgundy to blue (Khopkar et al., 2002).

Calcium carbonate ($CaCO_3$) is a naturally occurring inorganic biomaterial in the form of white solids, such as lime, marble, and calcite. This compound is formed from strong ionic bonds between calcium and oxygen atoms (Vironika, 2022). Magnesium carbonate is a chemical compound formed as a result of the reaction between magnesium and carbon dioxide gas, producing complex compounds such as MgO, CO_2, and H_2O, known as hydromagnecytes (Chrisayu et al., 2019). A buffer solution is a solution whose pH only changes slightly when a little acid or alkali is added, so it has the ability to maintain pH stability (Budiwati, 2019).

METHOD

Research Design

This research is an experimental research conducted in the laboratory. The method used is a quantitative method with a complexity analysis technique.

Research Time and Location

Sample collection was carried out in Sampuabalo Village, Siotopina District, Buton Regency, while the research process will be carried out at the Baubau Polytechnic Pharmacy Laboratory. This research is planned to take place from July to August 2024.

Tools and Materials

The equipment used in this study included 100 mL glass beaker, 50 mL burette, 50 mL glass bottle, 50 mL and 250 mL measuring flask, 250 mL erlenmeyer, 100 mL and 10 mL measuring cups, 50 mL volumetric pipettes, droppers, spatulas, as well as static and clamps. The materials used consisted of well water samples, aquadest, $CaCO_3$ 0.05M, $MgCO_3$ 0.05M, NRE indicators, pH 10 buffer solution, and Na_2EDTA solution.

Work Pose

Well water intake

Samples were taken from three wells located in lowlands, temperate plains, and highlands, each as much as 1 liter. Each sample is put into a glass bottle and labeled as a marker. The samples were divided into two categories: the first uncooked sample was labeled "R, S, T", and the second cooked sample was labeled "RM, SM, TM".

Standardization of Na_{2EDTA} Solution with CaCO3 Solution 0.01M MgCO3 0.01M (Rahayuningsih, 2017).

Once the tools and materials are prepared, 10 mL of $CaCO_3$ 0.01M and 0.01M $MgCO_3$ solutions are incorporated into the 250 mL erlenmeyer. Next, add 2 mL of pH 10 buffer solution and an EBT indicator (Erichrome Black T) to taste, around the end of the spatula spoon. Titration was carried out using a 0.05M Na_2EDTA solution until the color changed from burgundy to blue, and the volume of Na_2EDTA used was recorded.

Determination of Total Hardness (Rosvita, 2019)

Well water with lowlands

The tools and materials are well prepared. A total of 25 mL of uncooked well water is put into a 250 mL erlenmeyer, while 25 mL of cooked water is put into a separate erlenmeyer. Then, add 10 mL of pH 10 buffer solution and an NRE indicator to taste, around the end of the spatula spoon. Complexometry titration was carried out using a 0.05M Na_2EDTA solution until there was a color change from burgundy to blue, and the volume of Na_2EDTA used was recorded.

Well water with moderate plains

The tools and materials are well prepared. A total of 25 mL of uncooked well water is put into a 250 mL erlenmeyer, while 25 mL of cooked water is put into a separate erlenmeyer. Then, add 10 mL of pH 10 buffer solution and an NRE indicator to taste, around the end of the spatula spoon. Complexometry titration was carried out using a 0.05M Na_2EDTA solution until there was a color change from burgundy to blue, and the volume of Na_2EDTA used was recorded.

Well water with highlands

The tools and materials are well prepared. A total of 25 mL of uncooked well water is put into a 250 mL erlenmeyer, while 25 mL of cooked water is put into a separate erlenmeyer. Then, add 10 mL of pH 10 buffer solution and an NRE indicator to taste, around the end of the spatula spoon. Complexometry titration was carried out using a 0.05M Na_2EDTA solution until there was a color change from burgundy to blue, and the volume of Na_2EDTA used was recorded.

Data Analysis

Solution Standardization Calculation
CaCO3 (Wirdayawan, 2015)
V1 X M1 = V2 X M2
Information:
V_1 : Volume on_{2EDTA}
M_1 : Molaritas no_{2Edta}
V_2 : Volume $CaCO_3$
M_2 : CaCO 3 Molarites
CaCO3 Level Calculation (Wardhani, 2017)
Up to Kesadahan Total

$$= \frac{1000 \times VEDTA \times MEDTA \times BM\ CaCO3 \times fp}{V.\ Sample}$$

Information:
VolumeNa2EDTA : Titran volume
MolaritasNa2EDTA : Molaritas/Liter (mol/L)
BM CaCO3 : Molecular Weight 100 (gram/mol)

Solution Standardization Calculation
MgCO3(Wirdayawan, 2015)
V1 X M1 = V2 X M2
Information:
V_1 : Volume on_{2EDTA}
M_1 : Molaritas no_{2Edta}
V_2 : Volume $MgCO_3$
M2 : Molarites $MgCO_3$
Calculation of MgCO3 Levels (Wardhani, 2017)
Up to Kesadahan Total

$$= \frac{1000 \times VEDTA \times MEDTA \times BM\ MgCO3 \times fp}{V.\ Sample}$$

Information:
VolumeNa2EDTA : Titran volume
MolaritasNa2_{EDTA} : Molaritas/Liter (mol/L)
BM MgCO3 : Berat Malekul 84 (g/mol)

RESULTS & DISCUSSION

Research Results

A study has been conducted to determine the total hardness level of well water in Sampuabalo Village. Three samples of well water were taken, namely: (R) wells from lowlands, (S) wells from midlands, (T) wells from highlands, as well as (RM) cooked R well water, (SM) cooked S well water, and (TM) cooked T well water.

Before testing the water content of the well, the standardization of the Na_2EDTA solution is carried out first to determine the concentration of Na_2EDTA, so that the water content of the well can be calculated accurately. Standardization is carried out three times (triplo) to ensure the clarity and consistency of the results obtained. The results of the standardization of Na_2EDTA solution can be seen in the following table.

Table 1 Standardization of $Na_{2EDTA\ solution}$ with CaCO3 solution

No.	CaCO3 Solution	Volume CaCO3 (mL)	Volume Na2EDTA (mL)	Na $_{2EDTA\ Solution\ Concentration}$ (Molarity)	Color Change Results
1	I	10	1,3	0,05	The occurrence of a change in color from burgundy to blue
2	II	10	1,9	0,05	
3	III	10	1,5	0,05	
Average $Na_{2EDTA\ solution\ concentration}$				0,05	

Table 2 Standardization of $Na_{2EDTA\ solution}$ with MgCO3 solution

No.	MgCO3 Solution	Volume MgCO3 (mL)	Volume Na2EDTA (mL)	Na 2EDTA Solution Concentration (Molarity)	Color Change Results
1	I	10	1,9	0,05	The occurrence of a change in color from burgundy to blue
2	II	10	1,7	0,05	
3	III	10	2,4	0,,05	
Average Na2EDTA solution concentration				0,05	

Furthermore, titration was carried out three times on each well water sample to determine the total hardness level (CaCO3) and MgCO3 using the complexity method. The titration results can be seen in the following table:

Table 3 Determination of CaCO3 Levels in Well Water

No	Sample	Sample Volume (mL)	Volume Na2EDTA (mL)				Hardness Rate (mg/L) CaCO3)	Water Sadahn Standards	Color Change Results
			I	II	III	Average			
1	R	25	1,3	1,9	1,5	1,56	312	300 mg/L	The occurrence of a color change from burgundy to blue
2	S	25	1,5	1,5	1,3	1,43	286		
3	T	25	1,8	1,3	1,9	1,66	332		
4	RM	25	1,5	1,3	1,5	1,43	286		
5	SM	25	1	0,8	1	0,93	186		
6	TM	25	1,5	1,2	1,3	1,33	266		

Table 4 Determination of $CaCO_3$ Levels in Well Water

No	Sample	Sample Volume (mL)	Volume Na2EDTA (mL)				Hardness Rate (mg/L) CaCO3)	Water Sadahn Standards	Color Change Results
			I	II	III	Average			
1	R	25	1,3	1,9	1,5	1,56	262,08	300 mg/L	The occurrence of a color change from burgundy to blue
2	S	25	1,5	1,5	1,3	1,43	240,24		
3	T	25	1,8	1,3	1,9	1,66	278,88		
4	RM	25	1,5	1,3	1,5	1,43	240,24		
5	SM	25	1	0,8	1	0,93	156,34		
6	TM	25	1,5	1,2	1,3	1,33	223,44		

Information:

R : Well water with lowlands
S : Well water with moderate plains
Q : Well water with highlands
RM : Cooked water from the R well
SM : Cooked S well water
TM : Cooked T well water

Reaction

CaCO3 and Na2EDTA Reaction

CaCO3 + Na2EDTA → Ca(EDTA) + Na_{2CO3}

Complex ion formation reactions

Ca2+ -EBT → Ca2+EBT

Ca2+EBT + EDTA → Ca2+(EDTA) + EBT (biru)

Discussion

The purpose of this study is to determine the total hardness levels of $CaCO_3$ and $MgCO_3$ in well water in Sampuabalo Village using the complexity titration method. This research is important to ensure that the well water used by the people of Sampuabalo Village is safe, efficient, and does not cause technical or health problems.

The method used in this study is the complexity method, which is often chosen because of its ease in determining the titration endpoint. The basic principle of complexometry is the formation of complex ions in solution. The formation of complexes indicates a high level of solubility, where the complexes formed are metal complexes with EDTA. The titration endpoint is reached when all Ca^{2+} and Mg^{2+} ions have been bound by EDTA, characterized by a change in the color of the solution from burgundy to blue.

The procedure in this study began with sampling well water from Sampuabalo Village, which includes wells from lowlands, temperate plains, and highlands. The water sample is then put into a glass bottle and labeled as a marker. After that, the well water samples are cooked to a boil, and after boiling, the samples are put back into glass bottles. Furthermore, the research on the total hardness levels of $CaCO_3$ and $MgCO_3$ was carried out using the complexity titration method at the Baubau Polytechnic Pharmacy Laboratory.

The stages carried out in this study include the preparation of tools and materials to be used, followed by weighing $CaCO_3$, $MgCO_3$, and Na_2EDTA materials. Next, the $CaCO_3$ and $MgCO_3$ solutions are made using a beaker, and after dissolving, the solution is put into a 50 mL measuring flask. The Na_2EDTA solution is also made in a beaker until dissolved, then put into a 100 mL measuring flask, and the Na_2EDTA solution is transferred into a 50 mL burette. Standardization of Na_2EDTA solution was carried out using $CaCO_3$ and $MgCO_3$ solutions. A total of 10 mL of $CaCO_3$ and $MgCO_3$ solutions were put into erlenmeyer, then 2 mL of pH buffer solution of 10 and 30 mg (spoon tip) of NRE indicators were added. Titration was carried out with Na_2EDTA 0.05 M until there was a color change from burgundy to blue. To determine the total hardness level, a sample of 25 mL of well water was inserted into a 250 mL erlenmeyer, 2 mL of pH 10 buffer solution was added, and 30 mg (a spoon tip) of the NRE indicator. Titration was carried out little by little with Na_2EDTA 0.05 M until the color changed from burgundy to blue, and this process was carried out three times (triplo).

Although the concentration of Na_2EDTA of 0.05 M has been known theoretically, re-standardization is still necessary. This is due to the possibility of errors in the manufacture of solutions, measurement of solids mass, or solvent volume. In addition, the concentration of the solution may change due to evaporation, contamination, or deterioration of the quality of the reagent. Therefore, re-standardization is important to ensure that the Na_2EDTA solution really has the right concentration, so that the results of the analysis obtained can be considered accurate.

Boiling and heating is one of the methods that can be used to soften the hardness of water. The heating process can cause the release of carbon dioxide contained in the water, so the water will form insoluble $CaCO_3$ deposits. In this study, water was cooked at a temperature of 110°C until boiling. When the water boils, a $CaCO_3$ precipitate is formed that appears as a white precipitate. In Tables 4.1 and 5.1, it can be seen that the hardness level of water after cooking has decreased.

The water hardness level of $CaCO_3$ before cooking is 312 mg/L for lowlands, 286 mg/L for medium plains, and 332 mg/L for highlands. After cooking, the water hardness level decreased to 286 mg/L for lowlands, 180 mg/L for medium plains, and 266 mg/L for highlands. This shows that the level of water hardness after cooking has decreased. Meanwhile, the hardness level of $MgCO_3$ water before cooking is 262.08 mg/L for lowlands, 240.24 mg/L for medium plains, and 278.88 mg/L for highlands. After cooking, the water hardness level decreased to 240.24 mg/L for lowlands, 156.34 mg/L for medium plains, and 223.44 mg/L for highlanders.

Based on the results of the research that has been carried out, it was found that the well water in Sampuabalo Village has a difference in the hardness level of $CaCO_3$ and $MgCO_3$. The hardness level of $MgCO_3$ is lower than that of $CaCO_3$, this is due to the difference in molecular weight and the way the hardness equivalent is calculated. In standard measurements, $CaCO_3$ is considered an equivalent standard, so each gram of $CaCO_3$ contributes a higher hardness than each gram of $MgCO_3$. If there is a water source with different concentrations of Ca^{2+} and Mg^{2+} ions, the total hardness will be affected by the higher number of Ca^{2+} ions, so $CaCO_3$ tends to be the main contributor to the distress.

CONCLUSION

Based on the results of the research that has been carried out, it can be concluded that well water in Sampuabalo Village has a level of $CaCO_3$ hardness before cooking, which is 312 mg/L for lowlands, 286 mg/L for medium plains, and 332 mg/L for highlands. After cooking, the water hardness level decreased to 286 mg/L for lowlands, 180 mg/L for medium plains, and 266 mg/L for highlands. This shows that the level of water hardness after cooking has decreased. However, the hardness of water is still classified in the category of hard water. In addition, the water hardness level of $MgCO_3$ before cooking is 262.08 mg/L for lowlands, 240.24 mg/L for medium plains, and 278.88 mg/L for highlands. After cooking, the water hardness level decreased to 240.24 mg/L for lowlands, 156.34 mg/L for medium plains, and 223.44 mg/L for highlanders. Despite the decline, the hardness of water is still classified in the category of hard water.

The limitation of this study is that limited access to the equipment and materials needed to perform complexometry analysis is an obstacle in determining the total $CaCO_3$ (Calcium Carbonate) and $MgCO_3$ (magnesium).

ACKNOWLEDGMENTS

A big thank you to Mrs. Apt. Sri Yolandari, S.Farm., M.Si and Mrs. Hasty Hamzah, S.Si., M.Si as supervisor 1 and supervisor 2 who have provided a lot of assistance, direction and spent their time and thoughts in guiding the author from the beginning of the research until the completion of the preparation of this scientific paper. Thank you also to family, friends and friends who always provide support in compiling Scientific Papers and always patiently accompany the author in research.

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