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Analysis of Total Hardness Levels in Water Around the Trunojoyo Campus using the Complexometric Method

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ABSTRACT

Water hardness, primarily caused by dissolved calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, affects the suitability of groundwater for domestic use and may have adverse health and operational effects when concentrations are high. Indonesia's clean water quality standard (PERMENKES No. 492/MENKES/PER/IV/2010) sets a maximum hardness of 500 mg/L as $CaCO_3$. This study determined the total hardness of well water in three villages surrounding the Universitas Trunojoyo Madura campus (Telang, Gili Timur, and Labang) using complexometric titration with 0.01 M EDTA. Samples were collected by simple random sampling and titrated in triplicate. Results showed pronounced spatial variation: Telang village exhibited very high total hardness average 715.7 mg/L, Gili Timur had moderate hardness 146 mg/L, and Labang had low hardness 101.3 mg/L. The elevated hardness in Telang exceeds the national standard and likely reflects local geology (limestone contact and calcareous soils). We recommend pretreatment of well water used for drinking in areas with very high hardness.

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INTRODUCTION

Water is an essential component for life and the sustainability of ecosystems. Although Indonesia is known as a country with abundant water resources, the equitable distribution and quality of water is still a serious challenge [1];[2]. Water has an important role as a support and life support for plants, animals, and humans, as well as for human civilization itself. In addition, water is also a key element in supporting the sustainability of life [3]. Clean water is water that meets certain quality standards because it is free from physical contaminants, hazardous chemicals, and pathogenic microorganisms that have the potential to interfere with human health [4]. In Indonesia nearly 100 million people (38%) do not have access to proper sanitation, while 33 million (13%) live without improved drinking water. This condition is very worrying because adequate clean water is a very basic need [5].

Clean water scarcity is an increasing issue that affects human health, economic growth, and ecosystems in various regions around the world [6]; [7]. This is in line with research conducted by Ramadeandra [8], which shows that the availability of clean water is decreasing due to the reduction of infiltration areas that can be utilized as raw water sources. This is due to the large amount of development and exploitation of raw water sources, so that the amount of water that can be used for clean water distribution is decreasing. In addition, according to Djana [9], limited clean water sources in certain areas have caused serious problems for the health of the population living in these areas. Without effective planning and monitoring efforts, water quality can be jeopardized chemically or microbiologically, which has a direct impact on public health [10]. Therefore, it is imperative to ensure the availability and management of clean water to support people's lives.

Clean water demand refers to the amount of water required to meet the needs of the population in a particular region or area. There are several factors that influence the use of clean water by the community, including climate, population characteristics, industrial location, and water quality [11]. In addition, the level of human dependence on water is closely related to the fact that most of the composition of the human body consists of water. Meeting the need for clean water, especially for consumption, still faces challenges in the form of limited availability of water that is safe to drink, especially in the midst of rapid population growth [12]. Therefore, a hardness test can be carried out to determine the level of $CaCo_3$ in water that can be consumed and used in everyday life in accordance with PERMENKES No. 492/MENKES/PER/IV/2010.

Water hardness is a chemical property that affects the quality of clean water; the amount of calcium (Ca^{2+}) and magnesium (Mg^{2+}) in water determines the level of hardness [13]. The level of water hardness is determined by the concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions contained in it. Based on clean water and drinking water quality standards, the maximum allowable hardness limit is 500 mg/L, while the recommended minimum level is 75 mg/L [14]. Fresh waters usually tend to have high concentrations of calcium (Ca) and magnesium (Mg) ions, often exceeding 200 ppm in the form of $CaCO_3$. This is especially true in areas where water flows through limestone, resulting in high levels of hardness. High hardness can have an impact on daily water use, especially if it exceeds 100 mg/L, such as causing scale buildup on household appliances. If hardness exceeds 300 mg/L and is consumed in the long term, especially by individuals with weak kidney function, it can risk causing disruption to the kidney organs [15]. Previous research has been conducted by Nurisnaini & Purnamasari [16] on the water of Surabaya State University Lake using the titrimetric method, which resulted in a low hardness concentration level in the lake water, namely 97.65 mg/L. Amelia et al. [17], emphasizes that variations in calcium and magnesium ion levels affect the total hardness of water and determine the suitability of water for consumption and household use. Therefore, this study was conducted to determine the hardness level in the water used by the community around the Universitas Trunojoyo Madura campus using a more complex method, namely the complexometric method.

This study was conducted to determine the level of water hardness and provide information to the community around the Trunojoyo campus regarding the amount of hardness contained in well water used for consumption and daily needs, as no previous testing had been conducted, therefore, it was conducted to determine whether it complies with the standards set forth in PERMENKES No. 492/MENKES/PER/IV/2010, as well as to provide the author with insights into the hardness levels of well water around the Trunojoyo Bangkalan campus. The novelty of this study lies in the analysis of groundwater hardness levels in three villages (Telang, Gili Timur, and Labang) around Universitas Trunojoyo Madura, which have not been studied before, as well as comparing hardness levels between areas with different geological characteristics. In addition, the geographical location of the sampling site is close to the limestone production point, namely Bukit Jaddih, Bangkalan.

MATERIALS AND METHODS

Research Location

This research was conducted in April-June 2025 at the Chemistry Laboratory of the Faculty of Teacher Training and Education, Universitas Trunojoyo Madura, Bangkalan. The subject of this study is total water hardness, while the population and sample are groundwater from wells located around Universitas Trunojoyo Madura. The sampling technique used is simple random sampling, with the main consideration being the total hardness level at each location. A total of three well water samples were collected from Telang Village, Gili Timur Village, and Labang Village, which are marked with sampling points in Figure 1.

Figure 1. Location map of around the trunojoyo campus as a research object

Figure 1 shows the sampling locations for well water from the three villages, where sample location 1 is Gili Timur village, sample location 2 is Telang village, and sample location 3 is Labang village.

Materials and Equipment

The materials used in this study were 0.01 M EDTA solution, EBT indicator, 0.1 M NaOH solution, distilled water, pH 10 buffer solution, murexid indicator, and well water samples from around the Trunojoyo campus. The equipment used in this study were beakers, pipettes, pro pipettes, burettes, Erlenmeyer flasks, measuring cups, clamps, stands, pipettes, funnels, measuring flasks, and empty bottles.

Research Procedure

The research method used in this water hardness test an experiment with a quantitative approach, using complexometric titration as the main method. Complexometric titration was applied to determine the concentration of Ca^{2+} and Mg^{2+} ions in water samples through a series of laboratory procedures, such as adding reagents and observing changes in indicator color [15]. The research procedure is illustrated in the flowchart below:

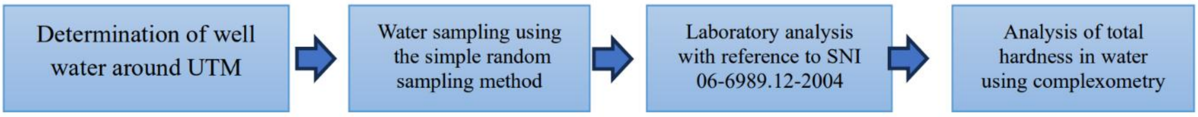

Figure 2. Flowchart of the research procedure for determining total hardness

This research procedure refers to SNI 06-6989.12-2004 concerning water hardness analysis. A total of 25 mL of sample was added to distilled water to make up 50 mL, then a pH 10 buffer solution and Eriochrome Black T indicator were added. Titration was then carried out with 0.01 M EDTA until the color changed from purple red to blue, indicating the end point of titration. Each sample was titrated three times.

Data Analysis

The study is descriptive quantitative in nature to measure the total hardness of well water around Universitas Trunojoyo Madura, namely in Telang Village, Gili Timur Village, and Labang

Village. Samples were taken randomly (simple random sampling). Testing was carried out using the complexometric titration method with EDTA, which reacts with Ca^{2+} and Mg^{2+} ions, indicated by a color change when the equivalence point is reached [18].

The calculation of total hardness in monitoring well water is performed using the total hardness formula. The formula used refers to Fajarwati & Efendi [19], as follows:

$$Ca^{2+} / Mg^{2+} \text{ (Mg/L)} = \frac{V\ EDTA\ x\ [EDTA]\ x\ Water\ [Ca/Mg]\ x\ 1000}{V\ sample} = \text{mg/L} \text{ ....[19]}$$

Description:

1. V EDTA: the volume of EDTA used during titration
2. [EDTA]: molarity of EDTA
3. Water [Subject]: relative atomic weight
4. 1000: L to mL unit conversion
5. V sample: volume of water sample used

The classification based on hardness leve

The classification of water hardness used in this study as cited by Fajarwati & Efendi [18]:

Table 1. Classification of hardness levels

Hardness Level	Mg/l $CaCO_3$
Hardness Level Soft Water	<50 mg/L
Medium Water	50-150 mg/L
Hard Water	150-300 mg/L
Very Hard Water	>300 mg/L

RESULTS AND DISCUSSION

This study was conducted through experiments to determine water hardness with the aim of calculating the level of water hardness in wells in three villages around the Trunojoyo campus using the complexometry method. In the complexometric titration process, a 0.1 M Na_2EDTA standard solution was used as the standard solution and EBT indicator to mark the end of titration. When the EBT indicator was added to the sample, the color of the solution changed to purple red. Furthermore, during titration with the 0.1 M Na_2EDTA solution, the solution's color, which was initially purple-red, changes to light blue. The results of water hardness calculations based on the volume of EDTA used in each repetition are presented in the following Table 2.

Table 2. Water hardness calculations for Telang Village

Ion	Experiment	Volume EDTA (mL)	[EDTA] (M)	Ar (g/mol)	Volume Sample (mL)	Results (mg/L)
Ca^{2+}	1	7.2	0.01	40	25	115.2
	2	8.7	0.01	40	25	139.2
	3	7.9	0.01	40	25	126.4
Average						126.9
Mg^{2+}	1	6.1	0.01	24	25	585.6
	2	6.3	0.01	24	25	604.8
	3	6.0	0.01	24	25	576
Average						588.8

This table shows the results of water hardness calculations in Telang Village based on Ca^{2+} and Mg^{2+} ion levels. The average Ca^{2+} level is 126.9 mg/L, while Mg^{2+} is 588.8 mg/L. The test was conducted through titration with 0.01 M EDTA on a 25 mL water sample. These results indicate that the water hardness in Telang is very high, which may be due to the high calcium content in the soil. This is consistent with the statement by [20], that groundwater has a higher hardness level because it interacts with limestone in the soil layers it passes through. Additionally, according to Nurullita [21], the high water hardness is caused by the presence of calcareous soil containing Ca(HCO) and $Mg(HCO)_2$. This is also supported by research by Tarigan [22], that the high hardness is caused by the presence of +2 valence ions, namely calcium and magnesium ions, which are dissolved from limestone, dolomite, and other minerals. Water hardness can also be caused by dissolved metals, such as divalent or multivalent cations like aluminum, barium, strontium, iron, zinc, and manganese [23].

Table 3. Water hardness calculations for Gili Timur Village

Ion	Experiment	Volume EDTA (mL)	[EDTA] (M)	Ar (g/mol)	Volume Sample (mL)	Results (mg/L)
Ca^{2+}	1	2.3	0.01	40	25	36.8
	2	2.8	0.01	40	25	44.8
	3	2	0.01	40	25	32
Average						37.9
Mg^{2+}	1	6.1	0.01	24	25	63.4
	2	6.3	0.01	24	25	63.4
	3	6.0	0.01	24	25	63.4
Average						63.4

This table shows the results of calculations of Ca^{2+} and Mg^{2+} ion concentrations in water samples from Gili Timur Village. The average Ca^{2+} concentration was 74.7 mg/L and the Mg^{2+} concentration was 71.3 mg/L, obtained through titration with 0.01 M EDTA solution against a 25 mL sample. These results indicate that the water in Gili Timur has moderate hardness with relatively balanced Ca^{2+} and Mg^{2+} content, making it suitable for daily use without serious adverse effects. According to Sahiddin [24], the primary causes of water hardness are calcium (Ca) and magnesium (Mg). Calcium in water typically combines with bicarbonate, sulfate, chloride, and nitrate, while magnesium in water combines with bicarbonate, sulfate, and chloride. The higher the concentration of calcium and magnesium ions in water, the higher the water hardness level, and vice versa.

Table 4. Water hardness calculations for Labang Village

Ion	Experiment	Volume EDTA (mL)	[EDTA] (M)	Ar (g/mol)	Volume Sample (mL)	Results (mg/L)
Ca^{2+}	1	2.3	0.01	40	25	36.8
	2	2.8	0.01	40	25	44.8
	3	2	0.01	40	25	32
Average						37.9
Mg^{2+}	1	6.1	0.01	24	25	63.4
	2	6.3	0.01	24	25	63.4
	3	6.0	0.01	24	25	63.4
Average						63.4

This table shows that the water in Labang Village has the lowest hardness among the three areas tested. The average Ca^{2+} ion concentration is 37.9 mg/L, while Mg^{2+} is 63.4 mg/L. These results were obtained from titration with 0.01 M EDTA solution against 25 mL water samples. The Mg^{2+} content remains higher than Ca^{2+}, but overall, the water hardness level is low. The low hardness in Labang Village can be attributed to the local hydrogeological conditions dominated by coastal alluvial aquifers, where rainwater infiltration occurs rapidly, resulting in relatively short contact time between water and limestone [25]. This results in suboptimal dissolution of minerals contributing Ca^{2+} and Mg^{2+} ions, leading to low total hardness levels. This finding is in accordance with research on multivalent cation interactions studied by Ajung et al. [26], which showed that the sensitivity of ion detection in aqueous systems is influenced by the matrix composition and the stability of metal ion complexation. Additionally, according to research by Thin [27], coastal alluvial aquifers like those in Labang may also experience cation exchange, where Ca^{2+} and Mg^{2+} ions are replaced by Na^{+} ions from sediments or seawater intrusion, contributing to reduced hardness. A similar phenomenon aligns with the findings of Razi [28], indicating that the combination of infiltration and local rock characteristics plays a significant role in determining water hardness levels.

Table 5. Comparing water hardness levels

Parameters	**Telang Water**	**Gili Timur Water**	**Labang Water**
Ca^{2+} level (mg/L)	126.9	74.7	37.9
Mg^{2+} level (mg/L)	588.8	71.3	63.4
Total Hardness	715.7	146	101.3

This table compares the water hardness levels in Telang, Gili Timur, and Labang based on Ca^{2+}, Mg^{2+} ion concentrations, and total hardness. Telang has the highest hardness level with a total of 715.7 mg/L. Gili Timur has moderate hardness with a total of 146 mg/L. Labang shows the lowest hardness level with a total of 101.3 mg/L. To visually support the quantitative data in Table 5, the following image shows the color changes observed during the titration of Ca^{2+} and Mg^{2+} ions from water samples collected in Telang, Gili Timur, and Labang villages. The variation in color intensity indicates differences in the concentration of hardness-causing ions in each sample.

Figure 3. Color changes of Ca^{2+} and Mg^{2+} titration results in Telang

Figure 4. Color changes of Ca^{2+} and Mg^{2+} titration results in Gili Timur

Figure 5. Color changes of Ca^{2+} and Mg^{2+} titration results in Labang

The test was conducted using a complexometric titration method with EDTA, which reacts with Ca^{2+} and Mg^{2+} ions, indicated by a color change when the equivalence point is reached. The reaction that occurs in this titration involves the formation of a stable complex between divalent metal ions (Ca^{2+} and Mg^{2+}) and EDTA (ethylenediaminetetraacetic acid) as a chelating ligand. The complex formation reaction can be written as follows:

$Ca^{2+}+H_2Y^{2-}\rightleftharpoons CaY^{2-}+2H^+$

$Mg^{2+}+H_2Y^{2-}\rightleftharpoons MgY^{2-}+2H^+$

EDTA in its deprotonated form (H_2Y^{2-} / Y^{4-} depending on pH conditions) forms a very stable coordinated complex with Ca^{2+} and Mg^{2+} ions; the formation constant (Kf) for metal–EDTA complexes is generally very large, so that titration is quantitative when performed at the appropriate pH conditions [29]. The formation of this complex is the basis for determining the concentration of ions causing water hardness because each mole of EDTA reacts stoichiometrically with one mole of divalent metal ions. In the SNI procedure used for determining total hardness, titration is carried out at $pH \approx 10$ using a pH 10 buffer and Eriochrome Black T indicator; this indicator turns red when it associates with free metal ions and turns blue when all metal ions have been complexed by EDTA (equivalence point).

Based on the visual observations above, Telang Village samples show a more intense color change, reflecting higher concentrations of Ca^{2+} and Mg^{2+} ions compared to Gili Timur and Labang. These qualitative differences are consistent with the quantitative results presented in Figure 6 and are further illustrated in the comparative graph below.

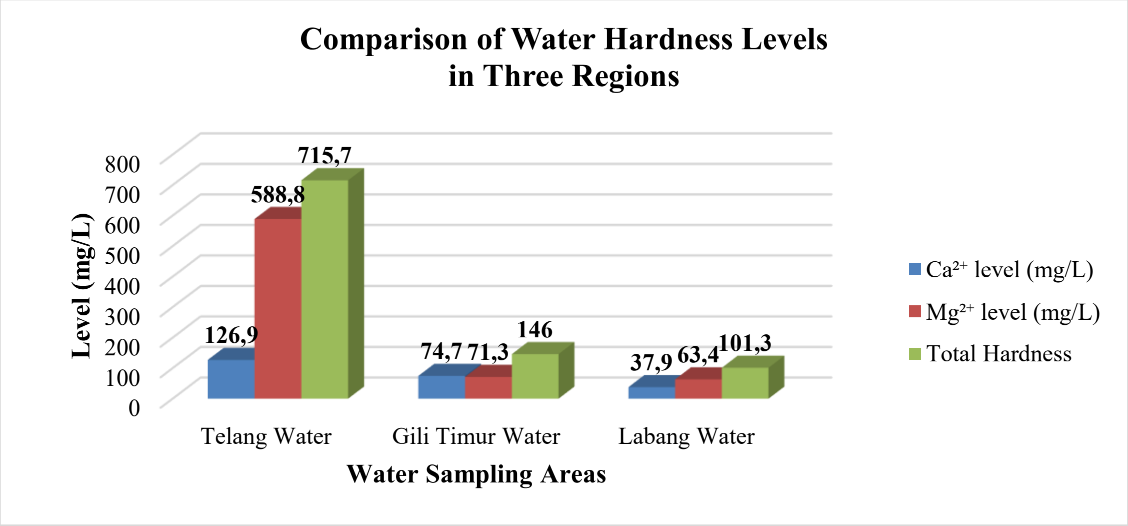

Figure 6. Graph comparing water hardness levels in three regions

The graph shows a comparison of water hardness test results in the three regions: Telang, Gili Timur, and Labang. Three types of data are displayed for each location, namely Ca^{2+} ion content, Mg^{2+} ion content, and total hardness (the sum of the two). This graph shows that Telang has the highest total hardness (715.7 mg/L), with Mg^{2+} content being much higher than Ca^{2+}. Gili Timur shows moderate total hardness of 146 mg/L with Ca^{2+} and Mg^{2+} content being almost equal. In contrast, Labang has the lowest total hardness of 101.3 mg/L, although Mg^{2+} is still higher than Ca^{2+}. This graph shows the differences in water quality characteristics in each region and indicates that geological factors greatly influence the ion content causing water hardness. Water hardness levels vary across locations, consistent with the statement by Sahiddin [24], that one of the factors influencing water hardness levels is the geological conditions around the area. Water flowing beneath the surface interacts with the environment it passes through. The type of rock present at a location is one of the geological factors contributing to water hardness levels in that area. The results of this study indicate that the water hardness level in Telang Village (715.7 mg/L) is much higher than the results of a study by Nurisnaini & Purnamasari [16], which found low hardness of 97.65 mg/L in the water of Lake Surabaya State University. This difference is likely due to factors such as geological conditions and different water sources. This is in line with the geographical location of Telang Village, which is close to the source of limestone, namely Bukit Jaddih. In addition, these results are also in line with the research by Herdini et al. [18], which showed the level of variation in Ca^{2+} and Mg^{2+} levels in well water in North Jakarta with a range of 120–680 mg/L $CaCO_3$. These findings reinforce that water hardness is greatly influenced by the mineral composition of the soil and rocks around the water source.

The high levels of Ca^{2+} and Mg^{2+} ions in water samples from Telang Village show a strong correlation with local lithological conditions. This area is known to be dominated by limestone and dolomite rocks that are easily soluble in water, especially under neutral to alkaline pH conditions. The dissolution of carbonate minerals such as calcite ($CaCO_3$) and dolomite produces Ca^{2+} and Mg^{2+} ions in groundwater, thereby increasing hardness values. This phenomenon is in line with the findings of Herdini et al. [18], who stated that the presence of carbonate rocks plays a significant role in the high hardness levels in well water. Thus, lithological variations between limestone, dolomite, and coastal alluvial areas can explain the differences in Ca^{2+} and Mg^{2+} levels found at the three research locations. Additionally, the geographical location of Telang Village is close to limestone sources, namely hills and coastal areas.

Indonesian Minister of Health Regulation No. 492/MENKES/PER/IV/2010 states that the standard for clean water quality is 500 mg/L, meaning that the water hardness in Telang Village exceeds the standard limit and does not meet the requirements. This tends to differ from the other two villages, namely Gili Timur Village and Labang Village, which have low levels of water hardness. In fact, hard water has a significant impact on health and even domestic use. Referring to Alisya et al. [14], the effects of hard water on health include cardiovascular disease (blockage of the heart's blood vessels) and urolithiasis (kidney stones). In addition, hard water also results in higher consumption of soap and detergent, because the chemical interaction between hardness ions and soap molecules causes the detergent properties of soap to be lost.

CONCLUSION

Based on the research results, the hardness levels of well water in three villages around the Universitas Trunojoyo Madura campus vary. Water in Telang Village has the highest hardness level of 715.7 mg/L, which exceeds the clean water quality standard limit of 500 mg/L. This high hardness level is caused by the calcium content in the soil and rocks in the area. Meanwhile, Gili Timur Village has moderate hardness with a total of 146 mg/L, and Labang Village has the lowest hardness with a total of 101.3 mg/L. These differences indicate that geological factors at each location significantly influence the concentration of ions causing water hardness, such as calcium (Ca^{2+}) and magnesium (Mg^{2+}). Therefore, for communities using well water as their primary water source, it is recommended to treat the water first. One alternative treatment method is to boil the water before use. In further research, it is recommended to use spectrophotometry or ion chromatography to analyze water hardness levels. The use of these tools can provide more accurate and specific data, thereby supporting further research on water quality in the area.

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