Research Article

Determination of Fluoride, Chloride and Nitrate concentration in ground water using ion selective electrode in Eastern Hararghe, Ethiopia

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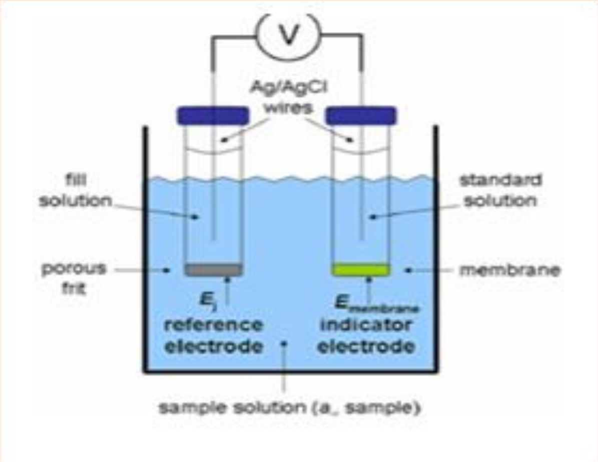
Abstract

A groundwater pollutant is any substance that, when it reaches an aquifer, makes the water unclean or otherwise unsuitable for a particular purpose. This study was designed to determine the concentration of F^-, Cl^- and NO_3^- using direct potentiometric ion selective electrodes (ISE) from six different areas of Eastern Hararghe zone ground water points. The mean concentrations of F^-, Cl^- and NO_3^- were found as 1.04±0.58-1.38±0.58, 37.15±0.50-95.49±1.53 and 1.90± 0.58-26.3±2.08 mg/L respectively and the values has no any considerable difference among the WHO permissible values. The turbidity values measured were in the range of 0.68±0.02 to 10.22±0.01 NTU. The high level of turbidity value on Kerensa (Kn) water recorded (10.22±0.01) was associated with disease causing bacteria's as a result of soil runoff during rainy season. The observed TDS in the present study was varied from 266± 1.00 to 608± 2.08 mg/L. All the mean values were agreed with the TDS values recommended by WHO for the selected water from the area. The electrical conductivity was varied from 396± 1.53 to 908± 3.52µS/cm and the value for all the water samples collected were higher than the World Health Organization permissible standards apart from Kulube (Ku) water sample. Therefore, on comparing the results against drinking water quality standards laid by WHO, it is found that some of the water samples in the area are less suitable for drinking purpose on the basis of certain physical parameters.

Keywords: Ion selective electrodes, World health organization, Eastern Hararghe.



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Introduction

Potentiometry is an electrochemical method in which the potential of an electrochemical cell is measured while little to no current is passed through the sample. When an ion selective electrode is used, the measured potential is related to the ion concentration in solution and a quantitative determination can directly be made [1]. The instrumentation used to perform potentiometry is straightforward and relatively inexpensive, consisting of an indicator electrode, a reference electrode, and a potential measuring device. Because specific ion electrodes measure activity and not concentration, a large amount of an inert strong electrolyte (e.g. nitrate ion) can be added to fix the ionic strength to a constant value. When the ionic strength is constant, the activity is constant and concentration can be accurately measured [2]. There are several advantages such as high selectivity, high sensitivity, quick analysis, low cost, wide variety of tested ions, and little sample size in ion selective potentiometric method [3].

Ion-selective membrane is the key component of an ion-selective electrode. Work of ion-selective electrode is based on the fact that there is a linear relationship between the electrical potential established between the ISE and reference electrode and the logarithm of activity (or effective concentration) of ions in the solution [1]. This relationship is described by Nernst equation:

$$E = E^{o} + \frac{2.303RT}{zF}\log a \qquad 1$$

Where, E is the total potential in mV developed between the sensing and reference electrode, z is the ion charge which is negative for anions, log(a) is the logarithm of the activity of the measured ion. The factor 2.303 RT/F has a theoretical value of 59 mV at 25 °C. The equation is valid for very dilute solutions or for solutions were the ion strength is constant. The activity is equivalent to the concentration in dilute solutions but becomes increasingly lower as the ionic strength increases. The activity (a) represents the effective concentration. The electrode responds only to free ions so it is important to avoid the formation of complexes that are meant to be measured. In this case, the complexation would lower the activity and therefore the electrode response. This is effectively the equation of a straight line:

$$y = mx + b \qquad 2$$

Where y is the measured electrode response (E) in mV, x = log (a), b is a constant ($E°$) value which is the intercept on the y axis, m = - 0, 0592/z is the electrode slope.

$$C_{i^-} = 10^{\frac{E-b}{m}} \qquad 3$$

Where C_i^- is the free ion concentration, E is the potential, m is the slope of the calibration curve and b is its intercept. To check the performance of the electrode particularly in the concentrations range of interest it is initially calibrated using standard solutions of the ion. Nitrates are an important source of nitrogen necessary for plants and animals to synthesize amino acids and proteins [4]. Most nitrogen on earth is found in the atmosphere in the form of nitrogen gas, N_2. Through a process called the nitrogen cycle, nitrogen gas is changed into forms that are useable by plants and animals. These conversions include industrial production of fertilizers, as well as natural processes, such as legume-plant nitrogen fixation, plant and animal decomposition, and animal waste [5]**.** Nitrate ions found in freshwater samples results from a variety of natural and manmade sources. Although nitrate levels in freshwater are usually less than 1 mg/L, manmade sources of nitrate may elevate levels above 3 mg/L and levels above 10mg/L in drinking water can cause a potentially fatal disease in infants called *methemoglobinemia*, or Blue-baby syndrome[6]. Monitoring nitrate (NO_3^-) in water has important implications to public health and environmental quality. Ion selective electrodes have potential for simple, rapid determination of NO_3^- concentrations in water among the analytical methods available. The use of ion selective electrodes has been limited due to interference by a variety of ions, relatively high detection limits, and short operational lifetimes [7].

According to Langmuir and Jacobson [8] chloride (Cl^-) and bicarbonate (HCO_3^-) were the chief interfering anions in most waters when using a commercially available liquid junction NO_3^- specific electrode. Chloride and fluoride are very reactive elements and because of that they easily bind to other elements. They belong to the group of halogens. Fluoride (F^-) is an important anion, present in water, air and food. Fluorides come naturally into water by dissolving minerals that contain fluor, such as fluorite (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$). Rocks rich in alkali metals have a larger content of fluoride than other volcanic rocks [9]. Small amounts of fluoride are vital for the human being, but it’s toxic when available at larger amounts. Fluoride levels in surface waters vary according to geographical location and proximity to emission sources. Surface water concentrations generally range from 0.01 to 0.3 mg/L [10]**.**

Human exposure to fluoride that varies from region to region is the largest single contributor to daily fluoride intake [11]**.** Due to this fact, daily fluoride intakes (mg/kg of body weight are based on fluoride levels in the water and water consumption per day per litter).The WHO maximum guideline value for fluoride is 1.5 mg/L [12].

The amount of fluoride present naturally in non-fluoridated drinking water is highly variable, being dependent upon the individual geological environment from which the water is obtained. It is well known that fluoridation of drinking water is an important tool in the prevention of tooth decay. Adequate fluoride ingestion is helpful to avoid caries, but over ingestion induces dental and skeletal fluorosis, which may result in malfunction of the bone and joint system [13]. The severity depends upon the amounts ingested and the duration on intake. Dental fluorosis is a condition where excessive fluoride can cause yellowing of teeth, white spots and pitting or mottling of enamel. Skeletal fluorosis is a bone disease exclusively caused by excessive consumption of fluoride [14].

Determination of chloride ions is important in many different fields such as clinical diagnosis [15] environmental monitoring[16] and various industrial applications [17]. Considering the fact that chloride channels play crucial role in physiological processes it is not surprising that miss regulation of chloride ions transport by these channels can cause serious disorders such as cystic fibrosis[18].Chloride ions in large quantities are present in sea water and sediments of the Earth's crust where it is associated with ions Na^+, K^+; Mg^{2+}. Chlorides are widely distributed in nature as salts of sodium (NaCl), potassium (KCl), and calcium ($CaCl_2$). Chlorides are leached from various rocks into soil and water by weathering. Exposure to chloride in air has been reported to cause a disease called cystic fibrosis [20]**.** Recommended thresholds for sodium chloride and calcium chloride in water are in the range 200–300 mg/L [19]. On the basis of a total obligatory loss of chloride of approximately 530 mg/day, a dietary intake for adults of 9 mg of chloride per kg of body weight has been recommended (equivalent to slightly more than 1 g of table salt per person per day) [18]**.** Chlorination as a method of water purification is used in 99% cases of the disinfection of municipal water. The chlorine can be added directly into the water. The taste of chlorinated water could be slightly acidic and it is probably because of the presence of chlorine is in the form of hypochloric acid. Permissible concentration of chlorine as a means of disinfections is up to 3 mg/L[19]. In the past two decades a number of researchers have sought to investigate analytical methods for chloride ions in a variety of samples, such as ion chromatography[20]**,** near-infrared spectrometry, [21] spectroscopy, [22] turbidimetric method, [23] and ion selective electrode method[24].

Among these, the development of potentiometric ion-selective electrode method has a wide range of applications in determining ions in water and other mediums due to ion selective electrodes are relatively free from interferences and provide a rapid, convenient and non-destructive means of quantitatively determining numerous important anions and cations [3]**.** However, previous studies have not dealt with determination of such anions using potentiometric ion selective methods around the area of Eastern Hararghe zone water resources, Ethiopia. Therefore, we are motivated to investigate the levels of some selected anions in the water resources and test the suitability for drinking purpose in relation to certain physical parameters.

Experimental

Apparatus and instruments

The instruments and apparatus used in this study were; Desiccators (SD-504, Japan), drying oven, Deionizer, pH and Ion meter (Jenway, model 3310, UK), conductivity meter (Jenway, model 4330, UK),Turbidity meter (Jenway, model 6035, UK).

Chemicals and reagents

Ammonium sulfate($(NH_4)_2SO_4$, 98% Sigma Aldrich, Germany) Sodium nitrate($NaNO_3$,99%, BDH ,UK),Sodium hydroxide (NaOH, 99%, Sigma Aldrich, Germany), Hydrochloric acid (HCl, 37%, Sigma Aldrich, Germany), Sodium fluoride (NaF,98%, Merk, Germany), Sodium chloride (NaCl, 99%, BDH,UK), glacial acetic acid (CH_3COOH, 99.9%, Sigma Aldrich, Germany, sodium citrate (99.5%, Aldrich, Germany), Sodium Acetate (CH_3COONa, 98%, BDH, UK). All the reagents used were analytical grade and used with no further purification.

Water sampling procedure

A total of 18 water samples were collected in 500mL pre-washed and cleaned polyethylene bottles from six different areas of eastern Hararghe zone (Chelenko, Kerensa, Haramaya, Langae, Kersa and Kulube) ground wells located in Eastern part of Ethiopia to deliver water representative of the sample and filled to the top to exclude air. Samples were labled with date and code as stated below. The sample was filtered off to remove suspended impurities, acidified by 1% acetic acid and stored at 4ºC till analyzed. Immediately after sample collection, pH, conductivity and TDS were determined. The turbidity of water sample was directly determined by the portable turbidity meter (Jenway 6035) at room temperature. Measurement of pH was carried out at room temperature by portable pH meter (Jenway 3310) after calibrated with pH 7 and 4 buffers. Conductivity and TDS were carried out at 25ºC by conductivity meter (Jenway 4330) after calibration with standard solution of 0.01N KCl.

Ch= Chelenko, Kn = Kerensa, Ha= Haramaya, La= Langae, Ke= Kersa, and Ku for Kulube

Calibration procedure for ion selective electrodes

pH /ISE meter (Jenway model 3310, UK) equipped with combination of the anions (F^-, Cl^- and NO_3^-) were employed for the determination of each ions in the samples and standards solutions. The liquid phase anion concentration was measured according to the procedure in the instrument manual. Potentiometric method was employed, where the potential was taken from pH /ISE meter equipped with combination of the ion selective electrodes and converted into concentration values using equation 3.

The ion selective electrodes were calibrated prior to the measurement of individual ion concentrations in samples for each experiment in order to determine the slope and intercept, which in turn are used to convert potential response to concentrations. Calibration plots were obtained by measuring of potential of six different sets of standard solutions of each ion ordered from low to high concentration. The meter reading was taken after a constant value has been attained that is drift < 0.1 mV/min.

Preparation of standards solutions

Flouride stock solution was prepared by dissolving 2.21g NaF in a 1000mL polystyrene volumetric flask with deionised water. Sodium fluoride has been previously oven-dried at 105°C for 1 hour and stored in a desiccators. The concentration of this stock solution is 1000 mg/L. Standard solutions of fluoride with concentrations 1, 5, 10, 15, 20 and 25mg/L in six 100mL polystyrene volumetric flask were prepared by appropriate dilution of the stock solution and addition of equal volume of the total ionic strength adjustment buffer (TISAB) in each solution. TISAB was prepared according to a recommended procedure (Agrawal *et al.*, 2003) as follows; 57mL of glacial acetic acid, 58.44g of sodium chloride, 0.29g of sodium citrate and 61.50g sodium acetate were added to 500mL of deionized water and allowed to dissolve and then the pH adjusted to 5.3 with 5M sodium hydroxide, and then made up to 1L in a volumetric flask with deionized water.

A 1000mg/L of chloride stock solution was prepared by dissolving 1.649g of NaCl in 1L deionised water. Sodium chloride has been previously oven-dried at 105°C for 1 hour and stored in a desiccators. Standard solution of chloride was prepared over the range of 20,40,60,80 and 100 mg/L. Recommended Ionic stabilization adjustment buffer i.e., $NaNO_3$(5M) was added (2% v/v) to both the standard solution and samples respectively.

To prepare 1000 mg/L of nitrate standard solution, 1.371g of $NaNO_3$ previously dried at 105°C for 1 hour and stored in desiccators was dissolved in 1L deionised water. Working standard solution of Nitrate was prepared over the range of 2, 4,8,12 and 16mg/L. Recommended Ionic stabilization adjustment buffer i.e., $(NH_4)_2SO_4$ (2M) was added (2% v/v) to both the standard solution and samples respectively.

Result and Discussion

Physical parameter studies quite important to get the quality and potability of drinking water. We analyzed physical characteristics of water samples collected from eastern Hararghe zone areas such as pH, total dissolved solids (TDS), Conductivity, and Turbidity.

Measuring the pH of water sample is important on determining the corrosivity of water because generally the lower the pH, the higher the level of corrosion [27]. The pH value of all the studied samples of water was agreed with the WHO guide lines (**Table 1**). Turbidity is one of the foremost parameter for the acceptability of drinking water quality. WHO, guidelines for turbidity are < 5 NTU. All natural water is turbid but generally surface water more turbid than ground water. The observed values in the studied samples for turbidity were varied from 0.68 ± 0.02 to 10.22± 0.01 NTU. Except for Kerensa water, the NTU values of all samples collected were found within the WHO limits (**Table 2**). Prior studies have noted that, the high level of turbidity is mainly associated with disease causing bacteria which might occur due to soil runoff during rainy season [26].

Table 1 WHO standards for some physical parameters at 25±2ºC

Sample No	pH	WHO limit (WHO,2003)
1	Cl-	200-300 mg/L
2	F-	1.5 mg/L
3	NO_3^-	50 mg/L
4	TDS	< 1000
5	Turbidity(NT U)	< 5(NTU)
6	Conductivity	< 500(µS)
7	pH	6.5-8.0

Table 2 Physical parameters measured (n=3) at 25±2ºC

Sample No	pH	Total dissolved solids (ppm)	Conductivity (µS)	Turbidity (NTU)
Ch	7.18± 0.025	608.33± 2.08	908.33± 3.05	1.86±0.03
Kn	6.65 ± 0.02	267.67± 2.08	530.33 ± 2.52	10.22±0.01
Ha	7.35± 0.02	391 ± 1.53	584.33± 1.53	1.57±0.04
La	7.29± 0.05	637± 2.52	951.67± 3.52	2.50±0.04
Ke	7.52 ± 0.05	553.33± 1.53	826 ± 3.52	0. 68 ±0.02
Ku	6.94± 0.03	266± 1.00	396.67± 1.53	1.37±0.02
WHO limit(2003)	6.5-8.0	< 1000	< 500	< 1

TDS from natural source have been found to vary with < 1000 mg/L [12]**.** The observed TDS in the present study was varied from 266± 1.00 to 608± 2.08 mg/L (Table 2). All the mean values were agreed with the TDS values recommended by WHO for the selected water from the area. The electric conductivity was varied from 396± 1.53 to 908± 3.52 microseimen per centimeter (µS/cm). The recorded TDS and conductivity were correlated by a conversion factor of 0.67 [28]. A value of 0.67 is commonly used as an approximation if the actual factor is not known [(TDS) ppm = Conductivity µS/cm x 0.67] and Electrical conductivity of water was directly related to the concentration of total dissolved solids in the water (Table 2). The Electrical conductivity of all water samples were higher than the WHO permissible value (<500 µS/cm) with an exception of Ku water.

Fluoride concentration in six drinking water samples was determined by direct potentiometry using ion selective electrodes (ISE) after the ISE was calibrated using standard solutions of fluoride prepared in series of concentration. From the data in **Figure 1**, it is apparent that the slope obtained from the graph were -57.42mV/dec as is expected from the Nernst equation for monovalent anion with a correlation coefficient of (R = 0.9991). The mean concentration of fluoride in real water sample and standard solution were determined from the calibration curve using equation 2. As shown from **Table 3**, the amounts of fluoride in six real water samples were in the range of 1.04±0.58 to 1.38±0.58ppm which is under the WHO permissible level in drinking water, 1.5 mg/L [12].

Chloride concentration was determined in six drinking water samples of the district of eastern Hararghe. The ISE was calibrated using standard solutions of chloride prepared in series of concentrations. The calibration data from **Figure 2** has shown that, the slope obtained (-57.01mVdec^{-1}) is in agreement with the expected value from the Nernst equation for monovalent anion with a correlation coefficient (R=0.9944). The concentration of chloride in water samples was determined from the calibration curve using equation 3. As **Table 4** shows, the amounts of chloride in six real water samples were in the range of 37.15±0.50 to 95.49±1.53 mg/L which are all in the permissible level of the WHO standards.

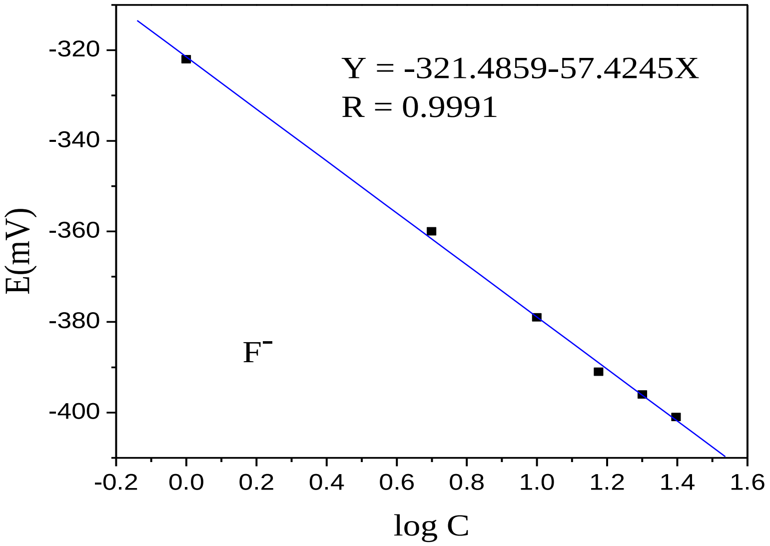

Figure 1 Calibration curve for fluoride analysis.

Table 3 Concentration of fluoride (mg/L) in six water samples (n=3)

	Ch	**La**	**Kn**	**Ke**	**Ku**	**Ha**
E(mV)	324	330	320	325	327	318
C(mg/L)	1.12±0.5	1.38±0.58	1.04±0.58	1.17±0.57	1.26±0.57	1.09±0.58

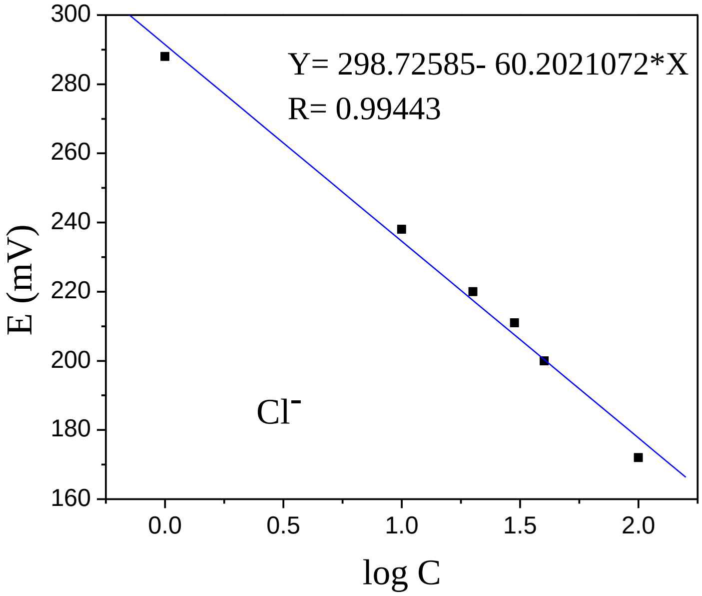

Figure 2 Calibration curve for chloride analysis.

Table 4 Concentration of chloride (mg/L) in six water samples (n=3)

	Ch	**La**	**Kn**	**Ke**	**Ku**	**Ha**
E(mV)	184	183	205	186	202	192
C(mg/L)	91.21±1.15	95.49±1.53	37.15±0.50	85.10±0.57	44.67±0.57	66.01±1.15

The concentration of nitrate in six drinking water samples was determined after the ISE was calibrated using standard solutions of nitrate prepared in series of concentration. The calibration curve obtained by applying direct potentiometry method is shown in **Figure 3**. It has been indicated that the slope obtained from the curve (-57.07mV/dec) is similar with the expected result from the Nernst equation for monovalent anion with a correlation coefficient (R = 0.9918). The concentration of nitrate in real water sample and standard solution were determined from the calibration curve. From the data in **Table 5,** we can see that the amount of NO_3^- in six ground water samples were 1.90±0.58 to 26.3±2.08 mg/L which are all with WHO recommended level. The maximum permissible concentration of nitrate in drinking water has been established as 50 mg/L [12].

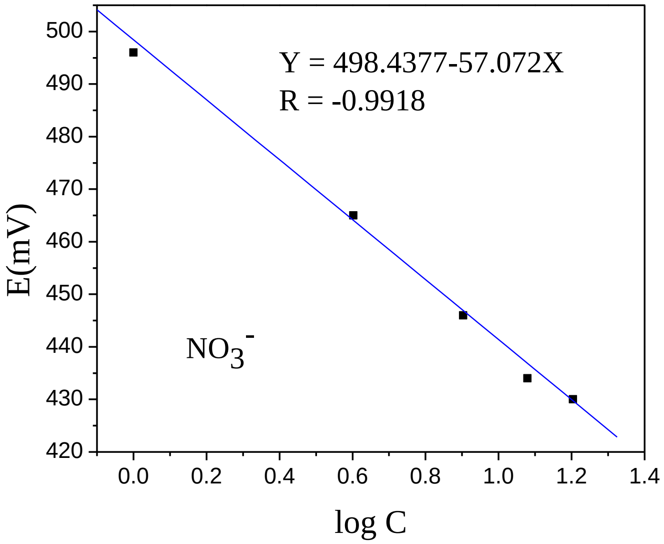

Figure 3 Calibration curve for nitrate analysis

Table 5 Concentration of nitrate (mg/L) in six water samples (n=3)

	Ch	La	Kn	Ke	Ku	Ha
E(mV)	417	482	480	467	449	469
C(mg/L**)**	26.3±2.08	1.90±0.58	2.09±0.58	3.48±0.577	7.24±1.53	3.24±0.58

Conclusion

The concentrations of fluoride, nitrate and chloride ions in the water samples were determined using potentiometric Ion Selective Electrode (ISE) techniques and some physical parameters such as conductivity, TDS and Turbidity were also tested to check the potability. The mean concentrations of fluoride, chloride and nitrates were found as 1.04±0.58 to 1.38±0.58, 37.15±0.50 to 95.49±1.53 and 1.90±0.58 to 26.3±2.08 mg/L respectively and all the results obtained were within the WHO recommended permissible standards. Based on the experimental data obtained, the turbidity values were 0.68±0.02 to 10.22±0.01NTU. High level of turbidity value on Kerensa (Kn) water recorded (10.22±0.01) might be mainly associated with disease causing bacteria's as a result of soil runoff during rainy season. Total dissolved solids (TDS) and electrical conductivity (EC) values obtained were in the range of 266± 1.00 to 608± 2.08 mg/L and 396± 1.53 to 908± 3.52µS/cm, respectively. However, the EC of all water samples collected were higher than the World Health Organization (WHO) permissible value (<500 µS/cm) aside from Kulube (Ku) water sample. Thus, some of the water samples are non-potable due to conductivity and turbidity parameters which are higher than the WHO standards. Therefore, a further attempt must be taken with more emphasis on studying microbiological test and some physico-chemical parameters to fully investigate the potability of the water around the area.

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