

Determination of Total Chloride/Bromide Ions and Total Hardness of Drinking Water of Uthal and LUAWMS, Lasbela, Baluchistan, Pakistan

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Abstract

Water is essential for life. Its quality directly affects plants, animals and humans. Contaminated water can not only be a cause of several diseases in humans but also can affect the growth and quality of plants. Drinking water of Lasbela university of Agriculture, water and marine sciences (LUAWMS) and Uthal city was tested for its total hardness and total chloride/bromide concentration. Mohr's method was used to determine the concentration of chloride and total hardness was measured in terms of Mg/Ca concentration using volumetric analysis. Samples were collected from five different sites of LUAWMS and Uthal. The total chloride and bromide content in samples of Uthal's bore, Uthal's hotel, Magsi hostel, Hingol hostel and Armabel hostel was 0.71 g/L, 0.3 g/L, 2.13 g/L, 1.77 g/L and 2.13 g/L respectively and total hardness in samples was 4.86 g/L, 4.86 g/L, 9.72 g/L and 11.42 g/L respectively. Samples taken from LUAWMS contain higher amounts of chloride and are harder than the samples from Uthal city indicating that Uthal's water is slightly better in quality. However, considering the WHO limits of both hardness and chloride content, the drinking water of the sites requires prior treatment as it exceeds the permissible limits.

Keywords: Chloride ions, Mohr's method, volumetric analysis, water quality, Uthal.

I. Introduction

Water is a necessity of life. One third of our earth is covered with water. Safe drinking water is crucial element for human's and organism's health but due to anthropogenic activities, agricultural wastes and industrial wastes being dumped into the water, its quality is not only being compromised but also leading towards the scarcity of water. According to Pakistan National Conservation Strategy, less precipitation, drought and under developed water resources raise water scarcity. The status of water supply is about 79% in Pakistan. During previous decade, it has been considered that the quality of ground water has varied and water is getting dirty rapidly leading to physical, biological, and chemical conditions. It has directly affected human's health. According to WHO, 80% of world diseases are caused due to insufficient sanitation, contamination, and inaccessibility of clean water (Iqbal et al., 2014). The high exposures of toxic metals being released in the environment cause bioaccumulation and bio-magnification which is disturbing the nature and contributing to high amounts of diseases in different species (Arain et al., 2009, Daud et al., 2017).

Given that the quality of water plays an important role in deciding the health of the people who are consuming it, parameters such as PH, TSS, TDS, chloride, magnesium, chromium, manganese, and cadmium are of great interest in drinking water (Hussain et al., 2014). Water which is free from physical, chemical, and biological pollutants is regarded as safe for drinking purpose. Existence of any of such parameters affect the quality of water and can be sometimes spotted by any change in color, taste, and odor clearly indicating it is not safe for drinking purpose (Ilyas et al., 2017). It is quite surprising that according to a community health studies report, about 50% of diseases and 40% of deaths occur because of poor quality of drinking water in Pakistan. However

exceptionally, 80% of people are utilizing safe drinking water in KPK. According to IUCN report, 60% deaths in Pakistan are caused due to diarrhea which is unfortunately the highest ratio in Asia (Daud et al., 2017). The main common sources of waterborne diseases are related to sewage water, municipal wastes, and industries wastes which are directly disposed into environment without any treatment. While excavation is another contributor of pollutant into ground water (Khan et al., 2018).

Recently water quality has been measured at several places in Pakistan. Khan *et al.* measured the water quality of Sindh. The samples were collected from 13 different districts which included Karachi, Hyderabad, Shikarpur, Mirpurkhas, Mithi, Tharparker, Sanghar, Thatta, Jacobabad, Gotki, Badin, Khairpur and Sukkar. They analyzed parameters such as color, odor, taste, alkalinity, bicarbonate, calcium carbonate, turbidity, chloride, conductivity, hardness as CaCO₃, Magnesium, PH, and microbial contamination. They used pour plate method for biological analysis. Results indicated its inappropriateness for drinking purposes. The samples contained high levels of microbial growth and pathogens in some cities like Badin, Gotki, Jacobabad, Khairpur, Mirpurkhas, Mithi, Tharparker, sangar and Thatta. However, in other cities water samples were fit for drinking purpose as they matched the international standard. (Khan et al., 2018). Memon et al. reported the quality of water taken from southern Sindh near Arabian sea. The samples were taken from different locations by random sampling technique from wells, shallow pumps and canals. Samples were analyzed for salinity, hardness, and microbes. Results showed the surface water was turbid and polluted with coli and soluble salts. Underground water was hard, alkaline and loaded with solids particularly, sodium. In the samples taken from wells, water contained a high concentration of sodium and iron. which came from the nearby sea. These pollutants cause kidney and skin problems. Diseases like gastroenteritis, diarrhea are also associated with dirty water utilization for drinking purposes (Memon et al., 2011). Hussain *et al.*, took random samples from tube wells, dug wells, springs, and hand pumps from Islampur, Swat, Pakistan. The results indicated the presence of solid particles in drinking water which could be related to geogenic sources of mélange zone rocks (Hussain et al., 2014).

Deeba *et al.* analyzed ground water quality in Punjab and Sindh. The samples were taken from sites that are normally utilized for drinking and other domestic purposes. The results showed that the international standards given by WHO was not being met by the samples. Some samples had excess microbial growth while others had excessive solid content in it making water unfit for drinking. The main reason reported for the contamination of water was anthropogenic activities (Deeba et al., 2019). Another study that was carried out in Jamshoro, Pakistan reported arsenic and physio- chemical parameters in both ground and surface water by Baig et al., in 2009. The results showed that both ground and surface water had higher concentration of arsenic than permissible limits of WHO. Ground water had slightly higher concentration of arsenic than surface water. The study suggested future work is required for pinpointing the source of arsenic (Baig et al., 2009). A similar study in Vihari, Pakistan determined hardness water that exceeded the permissible limit (Ghani *et al.*, 2019).

The quality of drinking water in Uthal, Lasbela has not been studied yet. This study reveals the total chloride/bromide content and total hardness in terms of Magnesium in drinking water of LUAWMS and Uthal.

2. Materials and Methods

All chemicals were bought from sigma Aldrich unless stated. Dry oven (Make: Eco cell) was used for drying chemicals and sterilizing the sampling bottles and portable battery operated Hannah pH meter was used at the sampling site and a benchtop pH meter (Make: Martini) was used for measuring the pH during titration.

Methodology is briefly summarized in Figure 1.

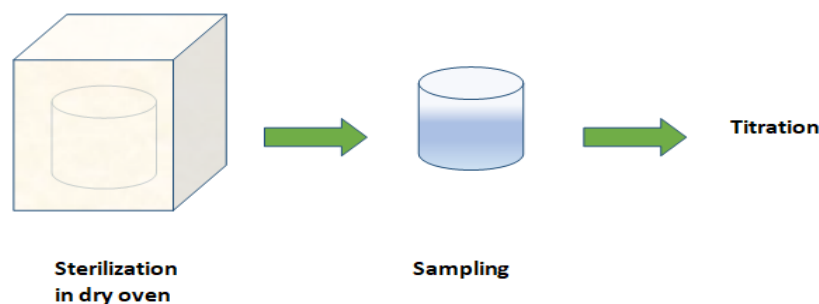


Figure-1: A schematic diagram showing the methodology

2.1 Study site and sampling

Samples were collected from several hostels of LUAWMS and from the Uthal city located in the Lasbela district of Baluchistan, Pakistan (Figure 2). 1L glass bottles were used for sampling. These bottles were sterilized in dry oven (eco cell) for up to 1.5 hours at constant temperature of 160 °C and were immediately sealed and stored in ice contained in small field box. From Uthal city, sample was taken from Uthal bore and a restaurant. The bore serves as a source of water supplied to local houses. A portable GPS was used for accurate location. A portable digital thermometer was used for measuring the water sample's temperature at the sampling site.

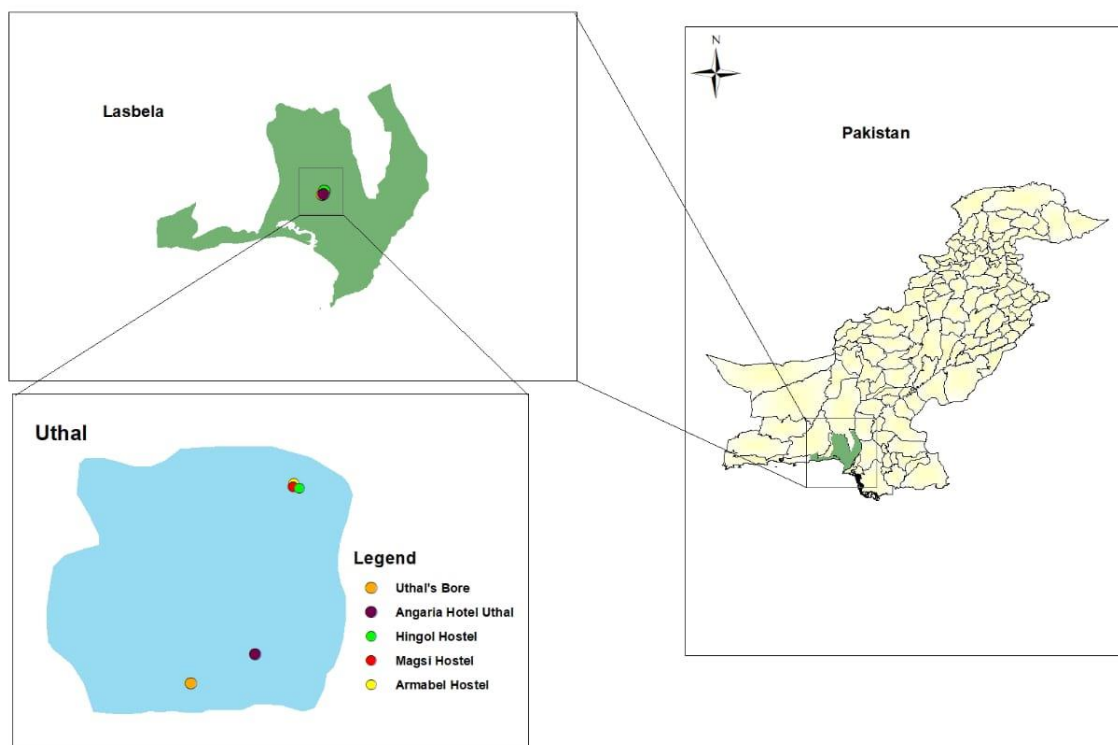


Figure-2: Map of study sites showing Uthal in the Lasbela district of Pakistan

The sampling technique was random and before sampling ethanol was used to eliminate the pollutants (iron, algae, etc.) from taps. Prior to collection, the water was left to flow for 2-3 minutes. After collection, temperature and pH was measured. The bottle was sealed with tape. In total, five samples were taken; two from Uthal city and three from LUAWMS university specifically from boys' hostels. The samples were stored in a field box containing ice and were brought to the laboratory for analysis. pH was measured using a calibrated bench top pH meter and samples were stored in a standard refrigerator. Table 1 summarizes the measurements taken at the sampling sites.

Table 1: Samples, their location and physical parameters

Sample No.	Sampling site	Location	pH at site	Temperature at site (°C)
1	Uthal's Bore	N 25° 48' 6.699" E 66° 37' 0.0012"	7.3	29
2	Uthal's hotel (Angaria)	N 25° 48' 24.0012" E 66° 37' 38.499"	7.6	26.5
3	Magsi hostel	N 25° 50' 6.2988" E 66° 38' 1.5102"	8	26.6
4	Hingol hostel	N 25° 50' 4.4982" E 66° 38' 1.2984"	8.2	26.3
5	Armable hostel	N 25° 50' 3.6996" E 66° 38' 4.9986"	8.3	26.1

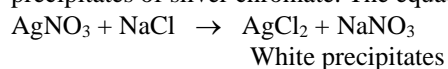
2.2 Qualitative Analysis

Odor, smell and color of water was observed. Qualitative analysis of chloride was done using silver nitrate and nitric acid in the sample. To the sample, a few drops of nitric acid and analytical grade silver nitrate solution was added. White precipitates show presence of chloride or bromide ions.

2.3 Quantitative analysis

2.3.1 Chloride content

Chloride content was determined using volumetric analysis specifically known as Mohr's method. The method has previously been used (Shukla and Arya, 2018). In this method a known concentration of silver nitrate is reacted with an unknown chloride sample in a slightly acidic solution until whole chloride is consumed. The end of reaction is marked by an indicator i.e. potassium chromate. In the presence of chloride ions, Silver nitrate tends to react with chloride first to form silver chloride and once all chloride has been consumed then it reacts with the chromate ions (indicator) to form silver chromate. As soon as all chloride has been consumed, the formation of silver chromate gives a visual indication of end point of the reaction in the form of orange precipitates of silver chromate. The equation for this reaction is



Silver nitrate absorbs moisture very quickly and gets oxidized in sunlight. Therefore, it is recommended to always make a fresh solution of known concentration before titration. The chemical should be pure and first dried. For standardization of silver nitrate (extra pure), it was initially dried in dry oven for an hour at 150 °C. Then 0.01 M solution was freshly prepared. Burette was filled with silver nitrate solution. 10 mL of NaCl solution was taken in a conical flask. 2-3 drops of potassium chromate were added. A few drops of nitric acid were added to maintain the pH between 7-9. Then the solution was titrated with silver nitrate until the solution in the flask turned orange. Initial and final burette readings were recorded for further calculations. For Blank, distilled water was used. Each titration was repeated for three concordant readings. The actual molarity of silver nitrate was calculated using the following equation

$$M_1 = M_2V_2 / V_1$$

Where M_1 = Molarity of silver nitrate, M_2 = Molarity of sodium chloride, V_1 = volume of silver nitrate used ($V_{\text{blank}} - V_{\text{NaCl}}$) and V_2 = volume of sodium chloride used. For measuring chloride concentration, 10 mL of sample was taken in a titration flask. 2-3 drops of potassium chromate were added in this solution. A few drops of nitric acid were added to maintain the pH. Then solution was titrated with silver nitrate until it turned orange.

Initial and final burette readings were noted. Titration for every sample was repeated to get three concordant readings. Chloride content was measured using the following equation

$$M_1 = M_2V_2 / V_1$$

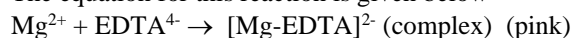
Where M_1 = Molarity of Cl^- , M_2 = Molarity of silver nitrate, V_1 = volume of sample used and V_2 = volume of silver nitrate used ($V_{\text{blank}} - V_{\text{sample}}$)

Concentration of Cl^- (g/L) = Molarity \times molecular weight (35.45)

2.3.2 Hardness of water

Hardness of water is measured by its total $\text{Mg}^{2+}/\text{Ca}^{2+}$ content. We used volumetric analysis to measure the Mg^{2+} concentration in drinking water samples. This requires standard Ethylenediaminetetraacetic acid (EDTA) solution and Eriochrome black T as an indicator. (Ghani et al., 2019). Many metal ions react with electron pair donors to form coordination compounds or complex ions. The formation of a particular class of coordination compounds, called chelates, are especially well suited for quantitative methods. A chelate is formed when a metal ion coordinates with two (or more) donor groups of a single ligand. Tertiary amine compounds such as ethylenediaminetetraacetic acid (EDTA) are widely used for the formation of chelates. Complexometric titrations with EDTA have been reported for the analysis of nearly all metal ions. Because EDTA has four acidic protons, the formation of metal-ion/EDTA complexes is dependent upon the pH. For the titration of Mg^{2+} , a pH of 10 or so is required so that the complex formation can be used for quantitative measurement. Basic pH is also required because erichrome black T only changes color between pH 7-11. This was done by using ammonia buffer. Ammonia buffer of pH 10 was prepared by mixing 0.1 M of Ammonium chloride with ammonia solution.

The equation for this reaction is given below



For the standardization of 0.01 M EDTA, it was taken in burette. 10 mL of 0.02 M solution of magnesium chloride was taken in conical flask. 5 mL of ammonia buffer was added in this solution to keep the solution basic. A few drops of Eriochrome black T were added and the solution was titrated with EDTA solution until it changed from blue to pink. Three concordant readings were taken for each sample. Blank titration was done using distilled water. Molarity of EDTA was calculated using the equation

$$M_1 = M_2V_2 / V_1$$

Where M_1 = Molarity of EDTA, M_2 = Molarity of Magnesium chloride, V_1 = volume of EDTA used ($V_{\text{blank}} - V_{\text{MgCl}_2}$) and V_2 = volume of MgCl_2 used.

Magnesium concentration of all samples was calculated from the volume of EDTA consumed by titrating the samples with standardized EDTA solution using Eriochrome black T and ammonia buffer. Following equation was used to calculate the molarity and concentration of Mg^{2+}

$$M_1 = M_2V_2 / V_1$$

Where, M_1 = Molarity of Mg^{2+} , M_2 = Molarity of EDTA, V_1 = volume of sample used and V_2 = volume of EDTA used ($V_{\text{blank}} - V_{\text{sample}}$).

Concentration of Mg^{2+} (g/L) = Molarity of $\text{Mg}^{2+} \times$ molecular weight (24.30)

3. Results and Discussions

3.1 Halide Detection (Chloride, bromide)

The qualitative analysis was done using the classic identification of halides. To the sample, a few drops of nitric acid and potassium chromate were added then silver nitrate was added. Any precipitates formed confirm presence of halides. The halides can be differentiated by the color of precipitates formed. Results obtained are given in table 2.

Table 2: Results obtained from qualitative analysis of water

Sample No.	Colour of precipitate	Result
1	White precipitates	Chloride present
2	White precipitates	Chloride present
3	Brown/white precipitates	Chloride may be present/silver nitrate possibly got oxidized
4	Creamy precipitates	Chloride may be present/bromide interference
5	White precipitates	Chloride present

The qualitative analysis showed presence of chloride ions in all samples. We quantified the total chloride/bromide and total hardness in terms of Mg^{2+}/Ca^{2+} content using volumetric analysis. Table 3 and 4 summarize the results obtained from titration and the volume of silver nitrate and EDTA used respectively. In case of any burette reading that exceeded the other trial readings, we ignored it and took average of the other two precise readings.

Table 3: Titration table for measurement of total Cl^-/Br^- in water

Analyte	Trial No.	pH	Initial burette reading (mL)	Final burette reading (mL)	Initial burette reading- final burette reading (mL)	Mean (mL)
Blank	1	7.6	11.3	12	0.7	0.7
	2	7.7	12	12.4	0.4	
	3	7.4	12.4	13.5	0.9	
Standardization of Silver nitrate with NaCl	1	7.2	0	19.5	19.5	19.6
	2	7.1	19.5	39.1	19.6	
Sample 1	1	8.3	0	7.9	7.9	9.4
	2	8.3	8.1	16.5	8.4	
	3	8	25.2	37.1	11.9	
Sample 2	1	8.2	0	24.7	24.4	20.3
	2	8.0	24.4	49.1	24.7	
	3	8.1	0	11.9	11.9	
Sample 3	1	8.8	13	16.9	3.9	3.9
	2	9.1	16.9	20.6	3.7	
	3	8.6	20.6	24.8	4.2	
Sample 4	1	8.7	0	4.5	4.5	4.7
	2	8.3	4.5	9	4.5	
	3	8.6	9	14	5	
Sample 5	1	8.5	0	3.7	3.7	3.7
	2	8.6	3.7	7.5	3.8	
	3	8.8	7.5	11.2	3.7	

Table 4: Titration table for measurement of total Mg^{2+}/Ca^{2+} in water

Analyte	Trial No.	Initial burette	Final burette	Initial burette	Mean
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		reading (mL)	reading (mL)	reading- final burette reading (mL)	(mL)
Blank	1	0	0.5	0.5	
	2	0.5	0.8	0.3	
	3	0.8	1.4	0.6	0.47
Standardization of EDTA	1	0	6.1	6.1	
	2	6.1	12.1	6	
	3	12.1	18	5.9	6
Sample 1	1	1.6	3.2	1.6	
	2	3.2	5	1.8	
	3	5	6.6	1.6	1.66
Sample 2	1	6.6	8.2	1.6	
	2	8.2	10.3	2.1	
	3	10.3	12.3	2	1.9
Sample 3	1	12.3	13.5	1.2	
	2	13.5	14.4	0.9	
	3	14.4	16	1.6	1.2
Sample 4	1	16	16.9	0.9	
	2	16.9	17.9	1	
	3	17.9	19.4	1.5	1.1
Sample 5	1	19.4	20.5	0.9	
	2	20.5	21.5	1	
	3	21.5	23	1.5	1.1

Chloride content of all water samples was high. According to WHO limits, chloride should not exceed 0.2 g/L. However, at LUAWMS, chloride concentration up to 2.13 g/L was measured. Chloride concentration in drinking water of Uthal city was lesser than the samples taken from LUAWMS. Hardness was measured as a total concentration of Calcium and Magnesium ions and the results showed that water is quite hard i.e. 11.42 g/L and exceeds the permissible limit of WHO i.e. 0.5 g/L. Hence drinking water of this area requires prior treatments to remove chloride and soften the water before it is consumed for drinking purpose. Table 5 summarizes the results and their comparison with WHO limits. Figure 2 and 3 show brief concentrations of chloride and total hardness in terms of Magnesium.

Table 5: Several parameters and their comparison with WHO limits (Kumar and Puri, 2012)

S. No.	Parameter	WHO limit	Results
1	Colour	-----	unobjectionable
2	pH	6.5-8.5	7.3-8.3 (within the limit)
3	Taste	-----	unobjectionable
4	Odour	-----	unobjectionable
5	Chloride	200mg/L (0.2g/L)	All samples exceed the limits.
6	Total hardness	500mg/L (0.5g/L)	All samples exceed the limit and are hard.

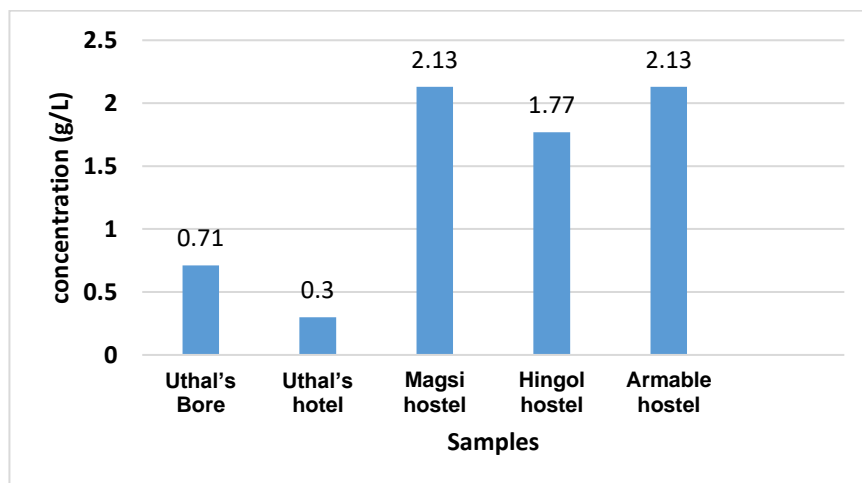


Figure 2: Total chloride/bromide concentration in g/L

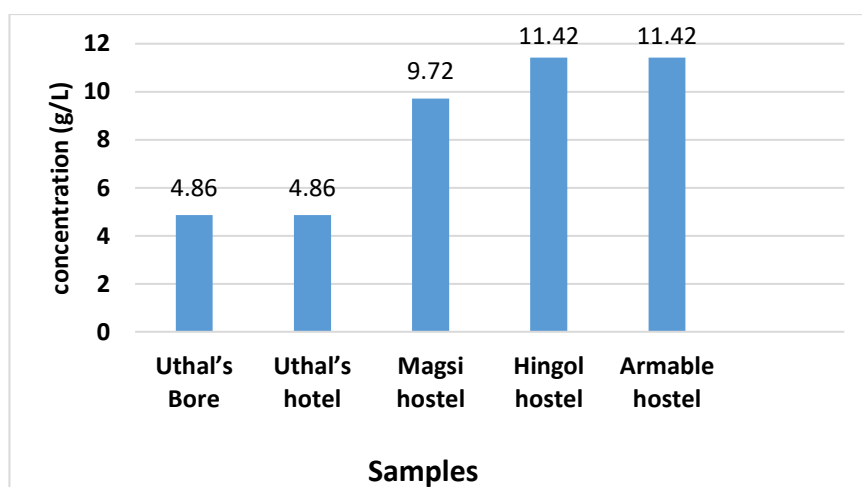


Figure 3: Total Mg²⁺/Ca²⁺ concentration in g/L

4. Conclusion

Drinking water of Lasbela university of Agriculture, water and marine sciences (LUAWMS) Uthal and Uthal city was tested for its hardness and chloride concentration. Mohr's method was used to determine the concentration of chloride and bromide. Total hardness was measured in terms of Mg concentration using volumetric analysis. Samples taken from LUAWMS had higher amounts of chloride and Mg than the ones taken from Uthal city. All water samples were hard and exceeded the WHO limit of hardness. The concentrations of total chloride and bromide in samples were 0.71, 0.3, 2.13, 1.77 and 2.13 g/L and total hardness in samples were 4.86, 4.86, 9.72, 11.42 g/L. The total chloride and bromide concentration of all samples except one taken from Uthal hotel exceeded the WHO limit. We therefore suggest that the drinking water requires prior treatment for hardness and the removal of chloride ions.

5. References

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