# A Fluidic Colorimetric Sensor Design for Water Hardness Detection

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Abstract-A new sensor design for detecting water hardness using complexometric and colorimetric concepts is presented in this paper. Calmagite, a metal ion indicator, changes color of a solution to wine red in presence of calcium  $(Ca^{2+})$  and magnesium (Mg<sup>2+</sup>) ions at pH 10. Ethylenediaminetetraacetic acid (EDTA) displaces the indicator from the metal-indicator complex after it is added to a solution and turns it blue. A red solution is transparent to a red light whereas nontransparent to a blue light and vice versa. A photodiode placed across the solution will give out a reading of voltage (V) variation across the diode depending on the amount of red or blue light passing through the solution and striking the photodiode. A sensor prototype is 3D printed with a channel embedded in it to hold water sample. Water hardness is detected based on visual inspection of color change of the sample and voltage change occurring when calmagite and EDTA are mixed to the sample. For a first-generation prototype, voltage variation of  $\sim 30\%$  and 13% for blue light and 6% and 74% in average for red light in comparison to the baseline, i.e., when neither calmagite nor EDTA is mixed to the water sample, is observed due to color change. Then, a second-generation prototype is printed, which shows improvement in voltage readings compared with the first generation. Transmittance and absorbance of the solution are computed using the voltage variation data recorded across the photodiodes. A calibration curve is then compiled by measuring absorbance of various concentrations of standard CaCO<sub>3</sub> solution, which is then used to predict the water hardness type of the water sample.

Index Terms-Fluidic, colorimetric, complexometric, water hardness, total hardness, calcium, magnesium, 3D printing.

## I. INTRODUCTION

WATER HARDNESS is of great concern to both domestic and industrial users. It is caused by compounds of calcium and magnesium, and by a variety of other metals [1]. As the concentrations of calcium ( $Ca^{2+}$ ) and magnesium (Mg<sup>2+</sup>) are usually greater than other alkaline earth ions (Group 2), hardness is equated to  $[Ca^{2+}] +$  $[Mg^{2+}]$  [2]. The amount of dissolved calcium and magnesium

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120 121 - 180 181 - 250 200 Mi 600 Miles PUERTO RICO 200 400 0 100 Miles 800 Mi 200 400 600 Kilometers Mean hardness as calcium carbonate at NASQAN water-monitoring sites during 1975 water year Colors represent site data representing streamflow from the hydrologic-unit rea.

(Map edited by USEPA, 2005) Fig. 1. Map of water hardness in the USA as a concentration of CaCO<sub>3</sub> [3].

in water determines how hard the water is. Water hardness is typically classified into four types - soft (0-0.6 mmol/L), moderately hard (0.61-1.20 mmol/L), hard (1.21-1.80 mmol/L) and very hard ( $\geq 1.81$  mmol/L). For example, a big portion of the Great Plains and Mountain West in the US has 'very hard' water while the majority of the Southeast US has 'hard' water as seen in Fig. 1 [3]. Hard water creates spot in glassware, build-up on pots, rings around the bathtub and toilet bowl and reduces efficiency of soap and detergents. Besides these, hard water also clogs pipes from households to industrial installations due to scale buildup which can lead to breakdowns and eventually costly repairs. In addition to all the above factors, too much calcium and magnesium in drinking water can be detrimental to human bodies [4]. Previous and current works in detecting water hardness include flowbatch photometric system [5], potentiometric sensor array [6], fluorescent molecular aptamer beacon [7], acoustic wave sensors [8] and so on. For example, the flow-batch photometric system uses the complexometric and colorimetric concepts but the system contains several components which need to be carefully integrated in order to perform the hardness screening. The proposed potentiometric sensor array system in [6] uses 7 ion-selective electrodes, a reference electrode and complex processing to determine calcium and total hardness of water. The electrodes used in the sensor array also have

CONCENTRATION OF HARDNESS AS CALCIUM CARBONATE, IN MILLIGRAMS PER LITER

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presence of multiple chemical substances. With all these factors taken into consideration, the above mentioned sensors may not be cost-effective and feasible to use in average households. Besides these, there are commercially available devices that can detect water hardness along with determining  $Ca^{2+}$  and  $Mg^{2+}$  concentration. However, these devices are expensive, bulky in size and require additional configuration to use. The primary motivation behind this effort is to investigate a small-sized, low-cost sensor design that has the capability to integrate essential components of the detection system into single entity, can easily detect and determine water hardness (total hardness), robust and cost-effective for consumers.

In this paper, we present a sensor that combines two well known concepts - complexometry and colorimetry to detect water hardness. Preliminary results on this have been reported in [9] and here we present detailed results on further work been done. A water sample is taken into a sensor prototype, which is 3D printed and mixed with a pH 10 buffer, a metalion indicator and finally titrated with a chelating ligand. A blue and a red Light-Emitting Diode (LED) are illuminated on one side of the prototype with two photodiodes being placed on the other side of it to sense the intensity of lights. During the mixing process, the color of the solution changes prompting voltage variations across the two photodiodes. Therefore, visual observation of the water sample's color change and variation in voltage readings across the photodiodes confirm presence of  $Ca^{2+}$  and  $Mg^{2+}$  responsible for water hardness.

A colorimeter can be used to detect water hardness and also the concentration of calcium and magnesium ions in a sample. However, commercially available colorimeters are in the range of hundreds to thousands of dollars. There are also test kits available commercially that contain multiple items including chemicals required to perform water hardness test which can eventually become tedious and confusing. On the other hand, single and/or multiple LED and various types of detector based absorbance sensors are well investigated and summarized in [10]. Beside this, 3D printing is a rapidly growing technology and is capable of printing intricate structures. Our proposed design uses LEDs and photodiodes and integrates them into one unit with the help of 3D printing and printed relatively at a low price. It will thus eliminate the use and handling of multiple items and most importantly chemicals. Our proposed sensor is not intended to perform comprehensive water hardness detection but act as a redundant unit in existing systems. For instance, we are targeting household monitoring of water hardness, an example being water softener. The sensor may be used in average households where consumers can install it with their existing water softener system, a prospective application area. The sensor can then indicate whether the water is hard or soft just by checking the total hardness threshold value of soft water, which is around 0.6 mmol/L or 60 mg/L. Based on the information, the consumer can determine whether to replenish their water softener system or not. In the following sections, we discuss about the theory of complexometry and colorimetry, detailed experimental procedure and finally elaborate on the results.



Fig. 2. EDTA - (a) Hexaprotic. (b) Tetraprotic.



Fig. 3. Chemical structure of calmagite.

## II. THEORY

Complexometry, also known as complexometric titration, is a titration based on complex formation [2]. Metal ions are Lewis acids, accepting electron pairs from electron-donating ligands that are Lewis bases [2]. When a ligand binds to a metal ion through more than one ligand atom, it is known as multidentate or chelating ligand. Ethylenediaminetetraacetic acid (EDTA) is a well-known chelating ligand or chelator. It is usually used as its disodium dihydrate salt [11]. It is a hexaprotic system designated by  $H_6Y^{2+}$ , where the highlighted acidic hydrogen atoms, Fig. 2(a), are lost upon metalcomplex formation [2].

$$Ca^{2+} + Y^{4-} \to CaY^{2-}$$
  $K_f = 5.01 \times 10^{10}$  (1)

$$Mg^{2+} + Y^{4-} \to MgY^{2-}$$
  $K_f = 4.9 \times 10^8$  (2)

However, the neutral acid is tetraprotic and represented as  $H_4Y$ . EDTA forms strong complexes with nearly every metal ion carrying more than unit positive charge [11]. The stoichiometry for EDTA is 1:1, which means it binds to metal ions like  $Ca^{2+}$  and  $Mg^{2+}$  in a 1:1 ratio. The stability of a metal-EDTA complex is dependent on the pH of the solution. The complexes of divalent metals are stable in ammoniacal solution [11]. By varying pH of a solution, it can be decided which metals will be titrated with EDTA and which will not. For  $Ca^{2+}$  and  $Mg^{2+}$ , the complexation reaction with  $Y^{4-}$  and corresponding formation constants  $K_f$  are given by (1) and (2) [12].

$$Ca^{2+} + HY^{3-} \rightarrow CaY^{2-} + H^{+} \qquad K'_f = 1.8 \times 10^{10} \quad (3)$$

$$Mg^{2+} + HY^{3-} \rightarrow MgY^{2-} + H^+$$
  $K'_f = 1.7 \times 10^8$  (4)

The formation constants with higher values mean that the above reactions will go to completion if EDTA exists in its completely deprotonated form. Moreover, the greater the stability of complexes the sharper the end points of the titration would be. To ensure that the titrant is in its completely deprotonated form, pH values greater than 12 are necessary [12]. However, at pH 12 both calcium and magnesium precipitate in the solution. Therefore, titration is generally carried out at pH 10 at which portion of EDTA is in HY<sup>3-</sup> form and

additional complexation reactions and conditional formation constants are given by (3) and (4) [12].

$$Mg^{2+} + HIn^{2-}(blue) \rightarrow MgIn^{-}(wine-red) + H^{+}$$
 (5)

[EDTA forms a weaker complex with  $Mg^{2+}$  than  $Ca^{2+}$ ,  $Ca^{2+}$  reacts with EDTA first]

$$Ca2+ + MgIn-(wine-red) + Y4- \rightarrow CaY2- + MgIn- (6)$$

[After all Ca<sup>2+</sup> is titrated, EDTA reacts with MgIn<sup>-</sup>]

$$MgIn^{-}(wine-red) + Y^{4-} \rightarrow MgY^{2-} + In^{3-}(colorless)$$
(7)

$$In^{3-}(colorless) + H_2O \rightarrow HIn^{2-}(blue) + OH^{-}$$
(8)

Both EDTA and  $Ca^{2+}$  and  $Mg^{2+}$  ions are colorless. Therefore, a visual indication is needed to detect the end-point in EDTA titration. The most common technique is to use a metal ion indicator. Metal ion indicators are compounds whose color changes when they bind to a metal ion [2]. There are several metal ion indicators available such as Eriochrome black T, Calmagite, Murexide, Xylenol orange and Pyrocatechol violet. Useful indicators must bind metal less strongly than EDTA does [2]. Both Eriochrome black T and Calmagite have been used to detect water hardness. However, Calmagite provides a sharper end point and has a longer shelf life than Eriochrome black T [12]. 1-(2-Hydroxy-5-methyl-1phenylazo)-2-napthanol-4-sulphonic acid or calmagite, Fig. 3, was proposed as a general purpose metallochromic indicator, though principally for calcium and magnesium, by Diehl and Lindstrom [11]. When calmagite is added to a water sample at pH 10, it will react with the  $Ca^{2+}$  and  $Mg^{2+}$  and the color of the solution will turn into wine-red. As EDTA is added, it will first react with any free  $Ca^{2+}$  and  $Mg^{2+}$  and then start to react with the colored complex. EDTA will effectively remove the metal ions from the indicator and tightly bind with them. As the metal ions unbind from the indicator, the color of the solution starts changing to blue which also indicates the end point of the titration. It is worth mentioning that when magnesium content in the solution is low relative to the calcium content, magnesium/EDTA is added to aid in getting a sharper end point [11], [12]. Moreover, the indicator binds too weakly to the Ca<sup>2+</sup> ions ( $K'_f = 4.4 \times 10^3$ ) and therefore to get a sharp end point Mg/EDTA is added into the solution [12]. The complete reaction process is given by (5)-(8) [13].

Spectrophotometry is any procedure that uses light to measure chemical concentrations [2]. Colorimetric analysis is adopted as it uses visible radiation to detect and determine the concentration of colored compounds in a solution. The intensity of light decreases as it passes through a solution. The amount of light passed through and absorbed by a solution is given by Transmittance (T) and Absorbance (A) respectively.

$$T = P/P_0 \tag{9}$$

$$A = log(P_0/P) = -logT \tag{10}$$

 $P_0$  = Initial intensity and P = Final intensity of light.

Absorbance is related to the concentration of the sample, the path length that light has to cover and molar absorptivity



Fig. 4. Three-dimensional printed first generation prototype.

of a particular substance. The relationship is expressed as Beers law and given as follows:

$$A = \epsilon bc \tag{11}$$

 $\epsilon$  in molar absortivity expressed in  $M^{-1}cm^{-1}$ , b is path length expressed in cm and c is concentration of the solution expressed in M (moles/liter).

## **III. EXPERIMENTAL SETUP AND PROCESS**

The prototype of the sensor was designed initially in Solidworks, a product of Dassault Systèmes SolidWorks Corporation located in Waltham, Massachusetts USA. Then it was printed using a 3D printer, Dimension Elite, which uses fused deposition modeling technology to print prototypes, Fig. 4. The material used to print the prototype was Acrylonitrile Butadiene Styrene (ABS), a common thermoplastic. The overall dimension of the prototype was 30 mm  $\times$  40 mm  $\times$ 15 mm. A 10 mm  $\times$  30 mm  $\times$  10 mm channel was embedded to hold the water sample. The prototype had two housings for two LEDs – one blue and one red, and two housings for two photodiodes. The path length that light had to cover in this prototype was 10 mm. A square opening was created for the photodiode housing and an iris was created for the LED housing. All the openings were closed off with transparent plastic slides appropriately cut to the size of the openings. Then epoxy was applied between the slides and the prototype body to prevent any leakage of the sample. A circular inlet and an outlet were created to inject sample in and out of the channel.

Before the experiment, 20 drops of distill water were taken into a 30  $cm^3$  clean vial and a small scoop of calmagite powder was mixed at pH 10. The color of the solution turned blue indicating absence of  $Ca^{2+}$  and  $Mg^{2+}$  ions. The experiment was performed in a semi-dark room to prevent the photodiodes detecting external lights. Two LEDs were inserted into the LED housings and connected to two separate 9V batteries. Then two photodiodes were inserted into the housings and the leads were connected to one Fluke brand and one Agilent brand digital multimeters respectively. Water sample was collected from a tap and preserved in a clean plastic cup. Then using 5 ml syringe water was poured into the channel. The LEDs were turned on and the top portion of the channel, completely open, was covered with a plastic slide colored in black. The slide was assembled by pasting a black tape on one side of a plastic slide. Voltage readings were taken from the multimeters and recorded, 0.50 V and 0.46 V for blue and red

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Fig. 5. Three-dimensional printed second generation prototype.

light respectively. Then 2 drops of pH 10 buffer and 2 drops of unknown concentration of calmagite solution, prepared by mixing distilled water with calmagite powder, were poured into the channel using separate clean plastic pipets. As soon as the solution was mixed with the water sample, it turned red. The top of the channel was covered with the black colored slide and voltage readings were recorded. The voltage across the photodiode detecting the blue light dropped by 0.11 V compared to the previous voltage reading whereas for the red light it only dropped by 0.03 V. After the measurement, the cover had been taken off and 2 drops of 0.2 M EDTA disodium salt (EDTA-Na<sub>2</sub>) solution, purchased from Sigma-Aldrich, were added to the sample. As soon as the solution was mixed, the sample turned blue. The opening of the channel was covered with the black plastic and voltage readings were taken from the multimeters. The voltage reading for the photodiode detecting the red light dropped significantly to 0.21 V. On the other hand, the voltage reading for the blue LED jumped to 0.44 V. After the readings were recorded, the lights were turned off and the photodiodes and LEDs were carefully taken out of their housings. The sample solution was then discarded and the prototype was rinsed in cold water for few minutes. The prototype was then rinsed again with distilled water and finally wiped with a TechniCloth® II nonwoven wiper to avoid contamination and affecting later tests. The same process had been repeated 9 more times and finally the voltage readings were plotted with standard deviation error bars. Ten new tests were repeated at a later time with variation in one test parameter. Previously, an unknown concentration of calmagite was used whereas during these 10 new tests a known concentration, 0.005 M, of calmagite had been used. During these tests, 4 drops of calmagite were needed instead of 2 drops during the previous 10 sets of test. In the first prototype of the sensor, the housings for both photodiodes were placed in a close proximity. During the experiments, it was observed that light from one LED would also hit the other photodiode. This was due to the close proximity of the housings, internal reflection of light inside the channel and refraction caused by the printing material. Therefore, a second generation device was designed to minimize the light being detected by the other photodiode in addition to the photodiode placed right across a LED. The 2nd generation prototype was built using a Dimension Elite 3D printer with an



Fig. 6. Experimental configuration with first generation prototype.

overall dimension of  $30 \text{ mm} \times 60 \text{ mm} \times 15 \text{ mm}$ , Fig. 5. It was printed using the same material as the 1st generation prototype, ABS. The inside channel of the prototype had a dimension of  $10 \text{ mm} \times 50 \text{ mm} \times 12 \text{ mm}$ . In the 2nd generation prototype, the input and output outlets were taken out, housings were placed apart by 16 mm and two wedge shaped blocks were placed in between the channel as a barrier for light to prevent detection by the other photodiode.

The experimental setup for the second generation prototype was similar to the first generation setup as shown in Fig. 6. Water sample was collected from a tap in the laboratory and stored in a plastic cup. Then water was poured into the channel with a 5 ml syringe and voltage readings were recorded for both photodiodes. Before the voltage reading was recorded, the top of the channel was covered with the black colored slide. The voltage readings for blue and red light recorded were 0.48 V and 0.44 V respectively. Then the cover was taken off and 3 drops of pH 10 buffer and 4 drops of 0.005 M calmagite solution were added to the water sample. As soon as the solution was mixed it turned into red. The cover was put back again on top of the channel and voltage readings were observed and recorded. The voltage for the blue light dropped to 0.39 V in comparison to the previous reading. On the other hand, the voltage for the red light dropped to 0.42 V, a change of 0.02 V only. After the readings were recorded, the cover was taken off again and 4 drops of 0.2 M EDTA solution were added to the water sample in the channel. The color then turned blue when EDTA was mixed with the sample. The voltage for the red light dropped by 0.26 V to 0.16 V whereas the voltage for the blue light jumped by 0.05 V. The sample was discarded and rinsed with cold water for few minutes. Then it was rinsed again with distill water to prepare it for another round of testing. The prototype was finally wiped with a TechniCloth® II nonwoven wiper and dried off. The process was repeated 9 additional times and color change was observed each time. After all tests were done, the voltage readings across the photodiodes were used to calculate transmittance and aborbance of the red and blue colored solution when calmagite and EDTA were added respectively. For example, transmittance of the red colored solution was calculated using equation (9) - dividing the recorded voltage data after calmagite was added to the mixture (sample water and pH 10 buffer) with the voltage data before calmagite was added to the mixture. Similarly,

### TABLE I

TRANSMITTANCE AND ABSORBANCE (MEAN) OF BLUE AND RED LED LIGHTS FROM FIRST TEN SETS AND SECOND TEN SETS OF EXPERIMENTS WITH THE FIRST GENERATION PROTOTYPE RESPECTIVELY AND FINALLY TEN SETS OF EXPERIMENT WITH THE SECOND GENERATION PROTOTYPE HOLDING SAMPLE (TAP) WATER

	Transmittance (%)		Absorbance	
	Blue	Red	Blue	Red
Water, pH 10 buffer, Calmagite	78.848	92.509	0.104	0.034
Water, pH 10 buffer, Calmagite, EDTA	86.409	50.127	0.065	0.362
Water, pH 10 buffer, Calmagite	70.039	93.881	0.157	0.027
Water, pH 10 buffer, Calmagite, EDTA	86.529	25.618	0.063	0.616
Water, pH 10 buffer, Calmagite	78.702	92.954	0.104	0.032
Water, pH 10 buffer, Calmagite, EDTA	88.602	40.812	0.053	0.414

transmittance for blue colored solution was calculated by dividing the voltage data after EDTA was added to the mixture (sample water, pH 10 buffer and calmagite) with the voltage data of sample water and pH 10 buffer mixture. Finally the mean was computed from the transmittance values for each 10 sets of experiment. Absorbance was calculated from transmittance using equation (10) and the mean was then computed for each 10 sets of experiment. The mean transmittance and absorbance of the 1st 10 sets and 2nd 10 sets of experiments with the 1st generation device and 10 sets of experiment with the 2nd generation device are summarized in Table I.

After all the tests were done with the sample water, 0.1 - 1.1 milli-molar (mM) standard CaCO<sub>3</sub> solutions were prepared from a 2 mM standard solution of CaCO<sub>3</sub> by diluting it with distilled water. Then for each concentration (0.1 mM, 0.2 mM, 0.3 mM and so on) of the diluted CaCO<sub>3</sub> solution the transmittance and aborbance were calculated in the following way. The channel was partially filled up with standard 0.1 mM CaCO<sub>3</sub> solution. Then 4-6 drops of 0.3 mM MgCl<sub>2</sub> solution and 4-6 drops of pH 10 buffer were added to the solution. The top of the channel was covered with the black plastic cover and voltage readings across the photodiodes were recorded. Then after adding 3-5 drops of 0.005 M calmagite solution, the mixture turned red and voltage readings were recorded. Finally, 1-2 drops of EDTA were added to the mixture, which then turned blue and voltage readings were recorded. This whole process was repeated 4 additional times and for all the prepared diluted concentrations of CaCO<sub>3</sub>. For concentration 0.7 mM and above, 8-9 drops of pH 10 buffer were mixed to the solution to observe color change when EDTA was added. Transmittance and absorbance were then computed in a similar fashion described earlier. The absorbance data for the red light was then used to form a calibration data set for our proposed sensor. Data from the experiments is shown and discussed in section IV.



Fig. 7. Voltage reading with error bars across photodiodes from first ten sets of experiment: (a) with water sample only, (b) with water sample, pH 10 buffer and calmagite, and (c) with water sample, pH 10 buffer, calmagite and EDTA for the first generation prototype.

## IV. RESULTS

Preliminary results on this work have been presented in [9]. Fig. 7 and Fig. 8 show the voltage readings with standard deviation error bars of the two photodiodes for two different sets of 10 experiments respectively for the 1st generation 3D printed sensor prototype. The horizontal axis of the graphs represents the experiment number and vertical axis represents the voltage readings recorded by the multimeters across the two photodiodes. Fig. 11 shows the color change when calmagite is added to the water sample at pH 10 and finally





Fig. 8. Voltage reading with error bars across photodiodes from second ten sets of experiment: (a) with water sample only, (b) with water sample, pH 10 buffer and calmagite and (c) with water sample, pH 10 buffer, calmagite and EDTA for the first generation prototype.

Fig. 9. Voltage reading with error bars across photodiodes from ten sets of experiment: (a) with water sample only, (b) with water sample, pH 10 buffer and calmagite and (c) with water sample, pH 10 buffer, calmagite and EDTA for the second generation prototype.

when EDTA is added to the sample. It should be noted that the black plastic cover was placed on top of the structure where the LEDs were located in order to prevent interference while capturing the picture. Fig. 9 shows the voltage readings with standard deviation error bars of the two photodiodes for the 2nd generation sensor prototype. In Fig. 9(c), the voltage readings for the red light are comparatively high for experiments 8-10; at least 0.08 V higher than the largest voltage drop among the first 7 experiments. The changes in the voltage drop caused the standard deviation error bar to become large compared to other measurements during the test. However, the overall trend on voltage drops from these 10 sets of experiment was comparable to the previous 20 sets of experiment with the 1st generation of prototype. The color change of the water sample during the experiments resembles the change during the first 20 sets of experiment for the 1st generation device, as seen in Fig. 11 (a) and (b), and hence not repeated here. From Table I, the variation in transmittance



Fig. 10. Calibration data set obtained by using absorbance of red light after EDTA is added to solutions with different concentration of  $CaCO_3$  (using the second generation device).



Fig. 11. (a) Red colored solution after calmagite is added. (b) Blue colored solution after EDTA is added to the water sample (using the first generation 3D printed prototype).

and absorbance from each 10 sets of experiment has been relatively consistent. However, the transmittance for red light is relatively low, when solution is blue, compared to blue light, when solution is red. Fig. 10 shows the calibration curve for the sensor with standard deviation error bars. As the concentration of CaCO<sub>3</sub> increases, the intensity of light detected by both the diodes decreases. The decreasing light intensity passing through the solution is thus captured by the gradual voltage variation across the photodiodes. The calibration data set is determined by taking into consideration the aborbance of red light when the solution turns blue after adding EDTA. Then basic curve fitting technique is used to plot the linear curve shown in Fig. 10, which also shows the equation and R-squared term. As previously mentioned in section II, EDTA first reacts with any free  $Ca^{2+}$  and  $Mg^{2+}$  ions and then reacts with the colored metal-indicator complex. By comparing the aborbance data of the red light from the 2nd generation device holding tap water with the calibration curve shown in Fig. 10, it can be predicted that the sample (tap) water falls under the 'very hard' ( $\geq 1.81 \text{ mmol/L}$ ) type water.

#### V. CONCLUSION AND FUTURE WORK

In this paper, we have presented a sensor that detects hardness in water sample based on concepts of complexometric titration and colorimetric analysis. The sensor prototype has been designed using 3D printing technology which houses two LEDs, blue and red, and two photodiodes. A channel embedded in the prototype holds water sample. After calmagite is added to the sample it turns red prompting voltage drop at the

photodiode detecting blue light. Then when EDTA is added to the solution it turns blue prompting voltage drop across the other photodiode. Therefore, we have shown through the experiments the presence of calcium and magnesium ions in the water sample, an indicator of water hardness. The 3D prototype is very shiny and reflects light internally and externally. Therefore, a new prototype has been designed to minimize light reflection. Experiments have been performed and similar trends in voltage readings across the photodiodes have been observed in comparison to the 1st generation prototype. Then a calibration curve has been obtained by measuring absorbance of various concentrations of CaCO<sub>2</sub> solution and from that curve the sample water's hardness has been predicted to be 'very hard'. As the concentration of solution increases, less light can pass through the solution causing gradual voltage drop. The gradual voltage drop thus indicates loss of transmittance, which in turn signifies the increase in absorbance.

The water hardness detection mechanism that we have discussed is based on observing color change of the solution and relating voltage drop due to the color change to absorbance of the solution. Our proposed sensor can be a costeffective addition to existing water softener systems in average households, one possible application out of many, where it will check whether the water is soft or not just by checking the threshold concentration value, 0.6 mmol/L, of soft water. The sensor is not intended to perform a comprehensive and precise water hardness detection as sophisticated equipments exist in big installations such as city water supply authority to perform rigorous and accurate detection and determination of water hardness. Future work will include choosing a dark colored 3D printing material to print the prototype, resizing the housings for both LEDs and photodiodes to prevent any misalignment, choosing a high resolution printer to avoid printing uneven surfaces and controlling test parameters more accurately. Besides these, a reliable mixing mechanism when pH 10 buffer, calmagite solution and EDTA are added to the water sample will be investigated. Presence of other metal ions such as copper, iron can interfere with water hardness detection. Therefore, techniques to neutralize the effect of other metal ions during water hardness detection will also be investigated. Even though calmagite solution is not deemed hazardous, a filtration option will be added to the sensor prototype in order to prevent mixing with the local sewage supply and causing further contamination.

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