

Optical Sensor to Detect Titration End Point to Evaluate Hardness of Drinking Water

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Abstract - Complexometric titration is a commonly used method to test hardness of water. Since small variation of colour is non observable to the naked eye in colorimetric method, it is advisable to use a sensor to monitor the variation of the signal throughout the titration process, which helps to detect the correct end point of the process. This paper discusses the ability of finding end point of titration using colorimetric method. Beer Lambert law was used for computing colour absorbance of the optical sensor. Three colours were transmitted via a solution one at a time, to detect the end point accurately. Less volumes of sample and titrant make an environmental friendly approach. The developed sensor is capable of detecting concentration of hardness from 100 mg/L to 1000 mg/L and automation of the device allows the process with no expert involvement.

Keywords: Colorimetric method, Titration end point, hardness, optical sensor

Nomenclature

- A - Absorbance
 ϵ - Molar absorptivity ($L \text{ mol}^{-1} \text{ cm}^{-1}$)
c- Concentration of the compound in solution (mg/L)
l - Solution path length (cm)
 P_{in} - Intensity of the light source (W/m^3)
 P_{out} - Intensity to the light detector (W/m^3)

1 INTRODUCTION

Measurement of hardness of water is important though there are fewer health hazards. However, long term consumption can lead to diseases such as nephrolithiasis (kidney stones), colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance (USGS 2016). Hardness in water causes to precipitate calcium and magnesium in boilers, kettles. However, long term consumption of such water directly impact on human health. According to many researchers (Chandrajith *et al.*, 2011; Dharmawardana

et al. 2014; Jayasumana *et al.* 2014), hardness is one of a supporting ingredient to produce complexes that cause the Chronic Kidney Diseases of Unknown etiology (CKDu). Dharmawardana *et al.* (2014) explain the possibility of drinking high ionicity of water effects on the kidney function. Apart from that the ground water used for drinking and domestic purposes may have unique fluoride, sodium and calcium ion concentrations, which could also be led to make complexities on fatal chronic kidney diseases (Chandrajith *et al.* 2011). The degree of hardness of drinking water has been classified in terms of the equivalent CaCO_3 concentration as shown in table 1. The SLSI 614:2013 standard of potable water recommends that the permissible level of hardness is 250mg/L, which implies that more than the said concentration is not suitable for drinking.

Table 1: Classification of hard water according to the CaCO_3 concentration

Classification	Hardness levels
Soft	0-60mg/L
Medium	60-120mg/L
Hard	120-180mg/L
Very Hard	>180mg/L

Note. From USGS Water-Quality Information, May 2016

The laboratory and portable instruments used for detection of hardness need skilled person to operate the instrument. Even with the presence of a skilled person, small variation of colour cannot be identified with the naked eye. The end titration point will change the reading of the concentration of ions. Therefore, this paper proposes a design of sensor for detection of hardness. The developed sensor will be embedded into an instrument enabling to obtain direct reading and minimize the cost as well as the time taken for the delivery of the samples to the laboratory.

2 REVIEW OF LITERATURE

Optical sensing can be used for many purposes. Omar *et al.* (2008) and Daraigan *et al.* (2007) illustrate a mechanism to calculate total suspended solids (TSS) in water. Transmittance and 90 degree scattering technique is used to evaluate the water quality of the system in Omar *et al.* (2008). This system consists of optical sensor with a fiber optic cable as the transmission media which is used in an experimental setup to evaluate the turbidity of water. The results has been obtained by emitting two wave lengths, 470nm (BLUE system) and 635 nm (RED system) tested with a known clay concentration for turbidity. Nitrate, sodium, calcium ions and heavy metal concentrations can be identified using electrodes and optrodes according to the studies carried out by Hanrahan *et al.* (2004), Thompson *et al.* (2014) and Pereira *et al.* (2007). Hanrahan *et al.* (2004) explains the

use of electrodes as the sensing element for environmental monitoring. There are various types of commercially available ion-selective electrodes such as Ca^{2+} , Ba^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Mg^{2+} , Cs^+ , NH_4^+ , Ag^+ , Na^+ etc. Ion Selective Optrode System (ISOS) of Thompson *et al.* (2014) is capable of identifying the ion concentration of K^+ , Na^+ , Ca^{2+} , and NO_3^- separately. The optrode, the sensing element consists of a Light Emitting Diode (LED) as an optical source, ion selective optrode film which produces the measurement of the ion concentration of a solution in the form of a colour change through spectrometer. Winkler (Furuya&Harada, 1995) and Karl Fischer (Koch *et al.* 2007) titrations are used to measure moisture content and dissolve oxygen respectively.

Complexometric titration, potentiometric titration, Atomic Absorption Spectrometry (AAS), Ion Selective Electrode (ISE) and optical test strips are few analyzing methods to detect concentration of hard water. Vahal *et al.* (2010) explains potentiometric detection via flow injection analysis (FIA) titrations to determine the Calcium and Magnesium in aqueous solutions. System is capable of determining pH value along with the hardness measurement. Optical test strip described in Capitán-Vallvey *et al.* (2003) uses ion exchange chromatography to detect the hardness of water. Life span of the optical test strip is one and half months when protected from the light. Paull *et al.* (1997) used graphitic as the stationary phase and o-cresolphthaleincomplexone as the mobile phase to separate ions in order to measure ion concentration through liquid chromatography. Filik *et al.* (2011) show that low concentration of calcium in water and milk can be identified by reflectance spectroscopy.

In laboratories the hardness is measured using Ethylenediaminetetraacetic acid (EDTA) solution with the Erichrome Black T indicator by detecting colour change in the solution. EDTA forms colour complexes with metal ions (Manahan, 1994). At pH 10, calcium and magnesium ions indicate colour change from red wine to blue in the absence of Ca^{++} and Mg^{++} ions as they make complexes using ionic Ca^{++} and Mg^{++} in the sample. This scenario was used in detecting the concentration of calcium and magnesium ions in colorimetric instruments. Bhattacharjee *et al.* (2013) has developed a sensor for detecting hardness using colorimetric concept. They captured colour change from red wine to blue through a photo detector, which gives appropriate titration point though voltage variation. In their study voltage variation of blue and red were 13% and 74% respectively. This paper presents the development of optical sensor to detect the end point of complexometric titration using three colours with further accuracy.

3 THEORY

Optical intensity was used as the sensing mechanism to detect the colour variation of the titration point. Absorption is defined as negative logarithmic of the transmittance as in equation (1).

$$A = -\log \left[\frac{P_{out}}{P_{in}} \right] \quad (1)$$

Incident power (P) is proportional to the photocurrent (I_p) of the detector as in equation

(2). Responsivity (R) is the proportional constant for a given range of wavelengths.

$$P = RI_p \quad (2)$$

Substituting the photo current which generated without solution ($I_{p(in)}$) and the photocurrent which generated after passing through the solution ($I_{p(out)}$) in equation (2), Absorption of the solution for a particular wavelength,

$$A = \log \left[\frac{RI_{p(in)}}{RI_{p(out)}} \right]$$

$$A = \log \left[\frac{I_{p(in)}}{I_{p(out)}} \right] \quad (3)$$

Beer - Lambert's law states that,

$$A = \epsilon cl \quad (4)$$

Hence,

$$c = \frac{1}{\epsilon l} \times \log \left[\frac{I_{p(in)}}{I_{p(out)}} \right] \quad (5)$$

According to the equation (5), generated current in the detector associates with concentration of an analyte in a solution. Also the reflection, scattering, refraction through the medium has to be minimized to obtain the linear relationship of logarithmic of the photocurrent variation to the concentration of the analyte.

Variations of photocurrent due to colours (or wavelengths) are used for detection of the titration point. Details of the detection mechanism is described in section 4.2.

4 METHODOLOGY

4.1 Reagents and standard solutions

Weight of 3.723g analytical grade disodium ethylene diamine tetra acetate dehydrate (also known as disodium salt of EDTA) was dissolved with 1000ml deionized water to prepare EDTA 0.01 M solution. pH 10 buffer was prepared dissolving 16.9g ammonium chloride with 143ml conc. ammonia and top up the solution to 250 ml with deionized water. Erichrome black T powder (Sodium salt of 1 - (1-hydroxyl - 2 - naphthylazo) - 5 - nitro - 2 - naphthol - 4 - sulfonic acid) indicator was prepared by grinding 0.2g indicator with 50g KCl and stored in a dark colour bottle.

In order to prepare the standard calcium solution (1ml = 1.00mg CaCO_3), weighted 1.000g anhydrous CaCO_3 is mixed with 1+1 HCl to dissolve CaCO_3 . 200ml of de ionized water was added and boiled for few minutes and left the solution to cool. Few drops of methyl red indicator was added to develop slight orange colour by adding 3N NH_4OH or 1+1 HCl as required. Prepared quantity was diluted to 1000ml with de ionized water (APHA 2005).

4.2 System methodology

Sensor consists of red, blue, and orange (absorption colour of blue) colour LEDs and phototransistors to detect colour intensity. In the tested set up, plastic cuvette was used to keep the solution in between LEDs and phototransistors. 5 ml of sample water, 0.2 ml of buffer solution (pH 10) and Eriochrome Black T powder were added and mixed to get cherry red /purple colour. Then EDTA solution was added and voltage variation was observed to check the end point of the titration which gives a blue colour.

Addition of EDTA was continued till the colour variation of red wine to blue indicates at the detector. End point of the titration was detected at the point where the voltage drops with orange and red colour lights and rises with blue colour light. When the detector identifies the blue colour the process was stopped and the amount of used volume of EDTA solution was measured for the calculation.

Total hardness is calculated using equation (6) (APHA,2005).

$$\text{Hardness (EDTA) as mg CaCO}_3\text{/L} = \frac{P \times Q \times 1000}{\text{mlSample}} \quad (6)$$

where:

P = ml titration for sample

Q = mg CaCO₃ equivalent to 1.00 ml EDTA titrant.

CaCO₃ equivalent to 1.00ml EDTA titrant (Q) was estimated by titrating 25 ml known concentration (1000mg/L) of CaCO₃ solution with 25 ml of EDTA solution. Using Equation (6), Q was computed as 1.

4.3 Reference Methodology

EDTA titration method was used to detect the total hardness of water samples. APHA (2005) testing procedure was adopted as the reference methodology. 25 ml of sample was mixed with deionized water to have a volume of 50 ml of sample for testing. This has been used to check the accuracy of the developed optical sensor.

4.4 Preparation for testing water samples

The buffer solution was added to the sample to be tested until the pH of the sample becomes 10. The 0.5 ml of EBT was added to the sample in order to develop wine red colour. The colour developed sample was used for titration to detect the end point.

5 RESULTS AND DISCUSSION

5.1 Validation of optical sensor

Small photocurrent variation needs to be analyzed to detect the endpoint. Even though the endpoint can be detected with a single colour variation, with small voltage variations it is difficult to identify the exact end point. Bhattacharjee *et al.* (2013) used two colour LEDs (red and blue) to detect the titration end point. Analysis of multiple signal variation patterns can be used to detect the exact end point further accurately. Accordingly absorbing colour of blue, which is orange was used to check the accuracy of the titration end point.

Optical sensor was tested with the standard solution (1000 mg/L) and the test results are tabulated in Table 2.

Table 2: Voltage variations of three colours with the added EDTA titrant volume with the standard solution

EDTA titrant (ml)	V(Orange)	V(Red)	V(Blue)
0ml (EDTA)	14.5	445	66.7
1ml (EDTA)+	17.1	472	91.1
1ml (EDTA)+	19.2	503	112.8
1ml (EDTA)+	21.3	515	138
1ml (EDTA)+	22.3	512	158.5
0.2ml (EDTA)+	23.5	490	159.3
0.3ml (EDTA)+	22.5	0.451	163.3
0.2ml (EDTA)+	20.1	0.362	174.8
0.3ml (EDTA)+	11.6	0.141	215.6
0.2ml (EDTA)+	10	0.114	210.8

At the beginning the voltages of three colours, increase with the addition of EDTA. A slight drop of the voltages of red and orange light was noted, in the instance of adding 4.5 ml of EDTA. A clear voltage difference was observed at the next drop of EDTA. The titration point was occurred at the point where 5 ml of EDTA added. Value of Q in equation (6) was computed as 1. The results revealed that the Q computed using developed optical sensor is similar to the reference method.

5.2 Testing water samples

Five water samples from Anuradhapura district were tested using the developed sensor. Tables 3 -7, present voltage readings of phototransistor according to the colour of the LED. Titration point was selected as described in section 4.2.

Table 3: Voltage variations of three colours with the added EDTA titrant volume with water sample 1

EDTA titrant (ml)	Output voltage (mV)		
	V(Orange)	V(Red)	V(Blue)
0ml (EDTA)	10.4	304	32.9
0.5ml (EDTA)+	8.8	248	25.1
0.5ml (EDTA)+	9.4	250	29.7
0.3ml (EDTA)+	8.6	195	34.2
0.3ml (EDTA)+	1.8	2.1	54.1

According to the data in table 3, sample 1 consumed 1.6ml of EDTA solution. The hardness of sample 1 was computed using equation (6) resulted as 320 mg/L. Similarly

hardness of sample 2, which consumed 1.8 ml of EDTA solution was estimated as 360mg/L. Highest variation of the voltage captured was in blue light in sample 2 that supports to detect exact titration end point.

Table 4: Voltage variations of three colours with the added EDTA titrant volume with water sample 2

EDTA titrant (ml)	Output voltage (mV)		
	V(Orange)	V(Red)	V(Blue)
0ml (EDTA)	11.9	322	46.2
0.5ml (EDTA)+	12.8	305	47.4
0.5ml (EDTA)+	13.3	308	53.8
0.3ml (EDTA)+	13.3	271	56.8
0.2ml (EDTA)+	9	149	68.8
0.1ml (EDTA)+	9	125	131.3

Table 5: Voltage variations of three colours with the added EDTA titrant volume with water sample 3

EDTA titrant (ml)	Output voltage (mV)		
	V(Orange)	V(Red)	V(Blue)
0ml (EDTA)	4.5	157	13.1
0.2ml (EDTA)+	3.4	88	9.4
0.2ml (EDTA)+	4.4	101	14.5
0.3ml (EDTA)+	4	88.5	15.8
0.1ml (EDTA)+	1.8	3.5	26

Hardness of sample 3 is low compared to other samples, which was calculated as 160 mg/L consumed 0.8 ml of EDTA solution. Red colour indicated the significant voltage variation to identify the endpoint of the titration.

Table 6: Voltage variations of three colours with the added EDTA titrant volume with water sample 4

EDTA titrant (ml)	Output voltage (mV)		
	V(Orange)	V(Red)	V(Blue)
0ml (EDTA)	18.6	445	80.5
0.5ml (EDTA)+	14.9	390	68
0.5ml (EDTA)+	16.8	390	78.6
0.3ml (EDTA)+	16.9	391	92.2
0.1ml (EDTA)+	14.4	270	97
0.1ml (EDTA)+	4.9	35	125.9

Sample 4 consumed 1.5 ml of EDTA solution and calculated hardness was 300 mg/L. Voltage variations of all colours were significant and supported the decision.

Table 7: Voltage variations of three colours with the added EDTA titrant volume with water sample 5

EDTA titrant (ml)	Output voltage (mV)		
	V(orange)	V(Red)	V(Blue)
0ml (EDTA)	11.4	333	25.3
0.5ml (EDTA)+	8.1	233	26.4
0.4ml (EDTA)+	8.9	220	27.5
0.3ml (EDTA)+	5.5	83.4	35.5

Sample 5 consumed 1.6 ml of EDTA solution which was used to calculate hardness of 240 mg/L. Voltage variation of the orange colour was not obeyed the variation properly at the beginning. Therefore blue and red supported to take the decision correctly for sample 5.

In the present study, calculated hardness using designed optical sensor of five samples were compared with APHA standard for hardness detection and summarized in Table 8. Samples 1, 2 and 5 were deviated from around 10%, 12% and 5% respectively. 100% accuracy was achieved by the two samples compared to the standard solution measurements. This indicates that the accuracy can be increased adding small drops of EDTA solution at a time. Testing was done manually to check the sensor responses.

In the sensor developed by Bhattacharjee *et al.* (2013) the error variations of red light voltage readings differ around 74%, while blue which is around 13%. In the present study, three colour optical sensor showed higher accuracy compared to the two colour optical sensor.

Table 8: Comparison of sensor design with the APHA standard procedure for hardness detection

Sample	Hardness (mg/L)	
	Designed sensor	APHA standard
1	320	372
2	360	404
3	160	160
4	300	300
5	240	252

Fig.1 shows the comparison of consumption EDTA volume in the designed setup and reference method. Contrast with the referenced procedure it shows a reduction of 20% of EDTA volume for a sample. As the sample size reduced the wastage also reduces. This is helpful in managing waste as the processors of recycles also cost money.

The sensor was closed and covered with a black casing to reduce the reflections within the unit and the influence of the environment light effects. Error variations are due to the manual testing of the sensor and it can be overcome when the sensor is automated in near future. The developed optical sensor measures hardness levels from 100 to 1000 mg/L, which generally indicates at the CKDu prevalence areas. Summary of the work shows that the developed sensor is in working condition and the testing is in progress for the improvements.

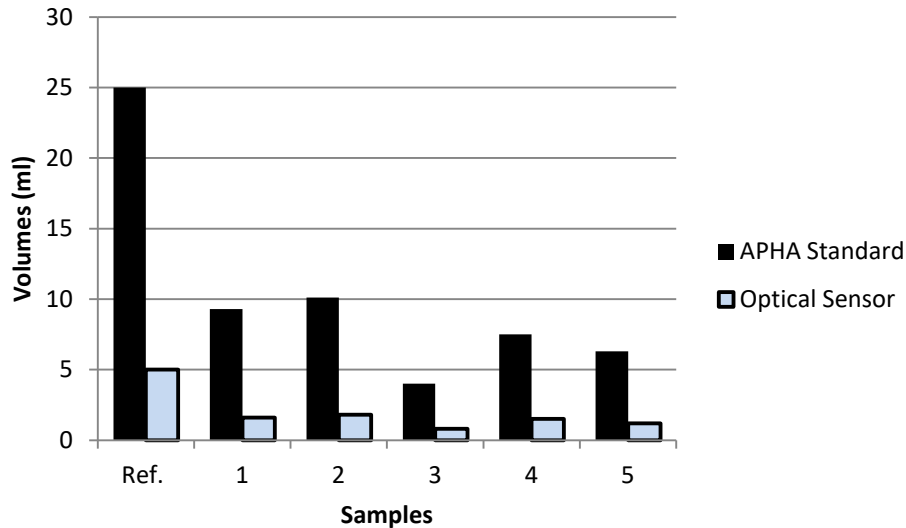


Figure 1: Volumes of EDTA consume in each sample with APHA standard procedure and optical sensor procedure

6 CONCLUSIONS / RECOMMENDATIONS

Three colour optical sensor is a successful method to detect titration end point to evaluate hardness of drinking water accurately. Hardness levels from 100 to 1000 mg/L can be measured using the designed sensor. Compared with the reference methodology the sample volume, EDTA volume and EBT powder consumption are reduced which makes an eco friendly approach. The low power consumption of the detector helps to use the sensor for a longer period of time. Improving user friendliness of the developed sensor through automation is under investigation. Automated system will help to test the water and advise the community whether to avoid or filter the water before drinking.

7 ACKNOWLEDGEMENT

The authors are thankful to Dept. of Agricultural and Plantation Engineering, Dept. of Civil Engineering, Dept. of Chemistry, Dept. of Electrical and Computer Engineering and National Water Supply and Drainage Board, regional support center, Anuradhapura for supporting this study and University Research Fund of The Open University of Sri Lanka for the financial support.

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