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A rapid method based on computer vision for the analysis of hardness and eutrophication levels in water bodies

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ABSTRACT

Water monitoring is essential in providing quality water to the communities which use water from nearby water bodies. In this study, a rapid method was analyzed. This method uses computer vision techniques to determine the total hardness (TH) and total phosphorus (TP) in five selective water bodies which include lakes and ponds. TH was determined by a color complex method using Eriochrome Black T indicator and TP was determined by another color-based method using a molybdate acid mixed reagent. These experiments were carried out in microwell plates of volume 5 mL. Images of the plate were acquired and regions of interests (ROIs) were obtained using suitable software and further subjected to image processing techniques to get their gray intensity values and RGB intensity values. These values were further fitted in to various linear regression models to derive equations for calculation of TH and TP concentrations. ROIs from sample water test images were analyzed in the same method to calculate TH and TP values which were further validated using standard testing methods. Results show that two out of three prescribed methods had a high precision with standard methods. Out of five samples tested, four samples showed that the water bodies have TP values in the range of 30–100 μg/L which is eutrophic in nature. One sample, a temple pond, exhibited a whopping 119 μg/L of TP which is considered as hypereutrophic. TH value of this sample was 227 mg/L which is considered as high hardness. Computer vision-based color processing method proved to be the best method for the rapid analysis of water quality parameters in situ.

Keywords: Computer vision; Total hardness; Total phosphorus; Eutrophication; Water quality

1. Introduction

Eutrophication is mainly responsible for the damage of freshwater bodies all around the world. Increased industrial pollution, agricultural pollution, and human activities around freshwater reservoirs pave way to the inorganic nutrients for reaching the water bodies [1,2]. Continuous accumulation of these nutrients may increase the risk of eutrophication in water bodies. In addition to this, there has been a problem of soil erosion in most parts of the world due to the loss of vegetation coverage. This erosion further supplies nutrients to the microalgae community in the water body.

Though there are many nutrients responsible for eutrophication, phosphate is considered the important nutrient and limiting nutrient of eutrophication. So, by controlling the concentration of phosphate ions in water bodies, the eutrophication can be minimized [3–5]. Furthermore, phosphate is also an important fertilizer for microalgae and small water plants. Inorganic phosphates are generally used as a fertilizer by agricultural industry. Also, many industries use inorganic phosphorus in their processing methods. These ions are released in wastewater in high concentration levels. The catchment area of small community lakes available

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in rural India are surrounded by agricultural fields. Thus, erosion by rain water carries excess inorganic phosphorus to the water bodies [5–7].

Environmental monitoring is an effective tool to assess eutrophication in freshwater bodies and salt lakes as well. There have been several approaches to monitor the water quality of these water bodies, but most of them require ex situ laboratory analysis studies to evaluate the degree of eutrophication and map their severity [8–11]. Collection and storage of water samples and consumption of high toxic chemicals to experimentally determine the phosphate levels in wastewater have become inevitable in the present system.

There is a need of an in situ eutrophication measurement system which can be handled by anyone easily [12]. The system, on the other hand, must be robust and accurate in predicting the concentration of indicator pollutant species. The analytical method should be a single step process and measurable with high precision and simplicity [13–15].

Computer vision has become a novel technique that finds applications in almost all branches of science [16]. It works in the concept of processing the images or signals from any system under test and analyzing their basic characteristics. Image analysis involves the determination of intensity values of red, blue, and green components of the image or gray component of the whole image [17]. These intensity values vary according to the color details in the image. Interestingly, many of the analytical techniques of water quality standards follow color-based reactions for the determination of concentrations. These colors were analyzed using a color measurement device called spectrophotometer and the technology of this device needs sophisticated facilities for the measurements to be made.

Determination of phosphorus concentration in water samples can be done using various methods which are mostly multiple step processes. The molybdenum blue method uses single reagent solution to measure the phosphorus concentration. Also, this method has unique advantages of good stability and negligible salt error correction [18].

Water quality monitoring also includes analyzing certain simple and important quality parameters like total hardness (TH) of the water samples. Hardness data of the water samples would give essential details regarding the accumulation of minerals in the water bodies. It is important to notice the concentration of these minerals (Ca and Mg) to understand the water contamination pattern of the water bodies. There is a simple and efficient method available to measure the hardness of the water samples by digital image colorimetry. Though the method uses toxic chemicals like Eriochrome Black T, the amount of these chemicals required to analyze the samples by this novel method is rather small, since the total volume of the each well in the microtiter plate is 300 μL. The discarded volumes of the spent chemicals are highly negligible.

This study deals with the determination of phosphorus concentration using molybdenum blue method in microwell plates and the images of these wells were analyzed using digital image processing algorithms to extract the color intensity data. These data were further processed and modeled to study the trend. Using model equations, the unknown concentrations were predicted and validated using standard analytical methods.

2. Materials and methods

2.1. Materials and chemicals

Stock solutions of 0.5 g/L of $CaCO_3$ and $MgCO_3$ were prepared with 0.1 mol/L of HCl and further diluted with distilled water. Phosphate stock solution was prepared by dissolving 0.1757 g of potassium dihydrogen phosphate in 1 L of distilled water. This was further diluted to give required concentration for standards. Buffer solution for hardness test was prepared with NH_4Cl (added and mixed till required pH) and aqueous NH_3 to the required pH of 10. Indicator for hardness was Eriochrome Black T, 1% solution in methanol. Hardness of all the water samples was analyzed by standard protocol of ethylenediaminetetraacetic acid (EDTA) titration method given by APHA [19]. To test hardness, a TH complexing solution was required. It was prepared by mixing 5 mL of 1% Eriochrome Black T and 100 mL of 0.01 mol/L of EDTA. For phosphate test [18] a mixed reagent was prepared by mixing 125 mL of 5 N sulfuric acid and 37.5 mL of ammonium molybdate (4% by weight), 75 mL of ascorbic acid solution (0.1 M), and 12.5 mL of potassium antimonyl tartrate solution (1 mg Sb/mL). For reference analysis, phosphate concentration was determined by stannous chloride method [20]. All the chemicals were purchased from SRL chemicals, Chennai, India.

2.2. Sample collection and storage

Water samples were collected from five different water bodies present in the vicinity of a 5 km circle of SSN College of Engineering, Chennai, Tamil Nadu, India. Samples of 1 L of water from two lakes, two ponds, and a stream were collected in thick clean and sterile glass bottles and stored immediately in icebox and transported to the laboratory. After the samples were allowed to reach room temperature, all the experiments were carried out immediately.

2.3. Experimental methods

All experiments were carried out using microtiter plates containing 12 wells having volume of 5 mL each. Prior to the testing of the samples, calibration experiments were carried out using standard solutions. For hardness tests, calibration experiments were done for concentrations of 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, and 250 mg/L by adding equal volumes of $CaCO_3$ and $MgCO_3$ solutions and diluting it further. Double distilled water was used as a blank solution. For phosphate calibration experiments, concentrations of 20–100, 150, 200, and 250 μg/L solutions were prepared by diluting the stock solution suitably. Double distilled water was used as a blank solution.

For hardness tests, about 3.5 mL of water sample was taken and 1 mL of TH complexing solution was added and mixed. In this mixture, about 0.5 mL of buffering solution was added and mixed again. The plate was left for 5 min for the color (blue) development to occur. After 5 min, the plate was placed in a foldable mini-studio box with inbuilt white LED light. Photos were taken using a 13 MP Moto G mobile camera and stored in BMP format for further analyses. For phosphate tests, about 4.2 mL of water samples were taken and 0.8 mL of mixed reagent was added and mixed well. The plate was hand agitated gently for 5 min. Then it was left

undisturbed for 10 min for the color to develop. A blue colored complex was formed in phosphate containing samples. Photographs were taken in the aforementioned manner and BMP formats were stored for further analysis.

2.4. Image treatment

The images captured were stored in BMP format. The region of interest (ROI) was selected using ImageJ® software and stored as separate image file in BMP format (383 × 383 pixels). These files were treated using Matlab 14.0® software. There were two types of treatments used to retrieve the data from images. First method was determining the gray value of the ROI images and second method was to determine the RGB values of the ROI images using ImageJ®. All the values were further used for different types of modeling. Equations were derived to determine concentration values from color intensity data.

2.5. Data analysis

Gray values obtained for the images of calibration experiment of hardness and phosphate concentration were fit in to a linear equation and coefficients were determined by using curve fitting tool box (Matlab 14.0®). The models derived using gray values are mentioned as Eqs. (1) and (2) as follows:

$$I_{\text{gray}} = a(\text{TH}) + b \tag{1}$$

$$I_{\text{gray}} = d(\text{TP}) + c \tag{2}$$

where *a*, *b*, *c*, and *d* are constants; I_{gray} are gray values of images; and TH and TP are total hardness and total phosphorus, respectively.

From RGB values obtained for the same experiments, average color intensity was determined using Eq. (3) as follows:

$$I_{\text{avg}} = \frac{I_R + I_G + I_B}{3} \tag{3}$$

where I_R, I_G, and I_B are RGB values of images. This average intensity values were fit in to a linear equation and coefficients were determined by similar method using Eqs. (4) and (5) as follows:

$$I_{\text{avg}} = e(\text{TH}) + f \tag{4}$$

$$I_{\text{avg}} = g(\text{TP}) + h \tag{5}$$

where *e*, *f*, *g*, and *h* are constants and I_{avg} is average color intensity.

A multivariate regression analysis was carried out for the RGB values of the images obtained during calibration experiments and a regression model was developed to determine concentration using RGB values. These models are mentioned in Eqs. (6) and (7) as follows:

$$\text{TH} = a_1 + a_2 I_R + a_3 I_G + a_4 I_B \tag{6}$$

$$\text{TP} = b_1 + b_2 I_R + b_3 I_G + b_4 I_B \tag{7}$$

where *a* and *b* are constants.

TH and TP concentration values of water samples collected were determined using all these three models and were compared and validated using reference analysis method.

2.6. Samples and methods

Various samples of water used in this study and methods of study are denoted as mentioned in Tables 1 and 2. Degree of hardness and eutrophication levels were determined as per Table 3 [21]. Fig. 1 shows the overview of the steps involved in this research work.

3. Results and discussion

3.1. Calibration studies

The calibration studies were done for both TH and TP at concentration levels of 20, 40, 60, 80, 100, 120, 140, 160,

Table 1
Water samples and their sources (types, names, and description of surroundings)

Sample no.	Type of water body	Name of water body	Remarks
1.	Lake	Kalavakkam lake	Surrounded by agricultural fields and a hamlet
2.	Lake	Thaiyur lake	Surrounded by agricultural fields and a hamlet
3.	Pond	Kannagapattu pond	Surrounded by barren land and a hamlet
4.	Pond	Thiruporur temple pond	Surrounded by busy market and a town
5.	Stream	Thaiyur stream	Surrounded by a small residential block and barren land

Table 2
Methods used to determine total hardness and total phosphorus

Method	Description
M1	Total hardness by APHA, 2005 [19]
	Total phosphorus APHA, 2000 [20]
M2	Based on gray values of images
M3	Based on I_{avg} values of images
M4	Based on multivariate regression model derived from RGB values of images

Table 3
Degree of hardness and level of eutrophication as per standards

Degree of hardness	Total hardness (mg/L)	Eutrophication level	Total phosphorus (μg/L)
Soft	0–60	Oligotrophic	5–10
Medium	60–120	Mesotrophic	10–30
Hard	120–180	Eutrophic	30–100
Very hard	>180	Hypereutrophic	>100

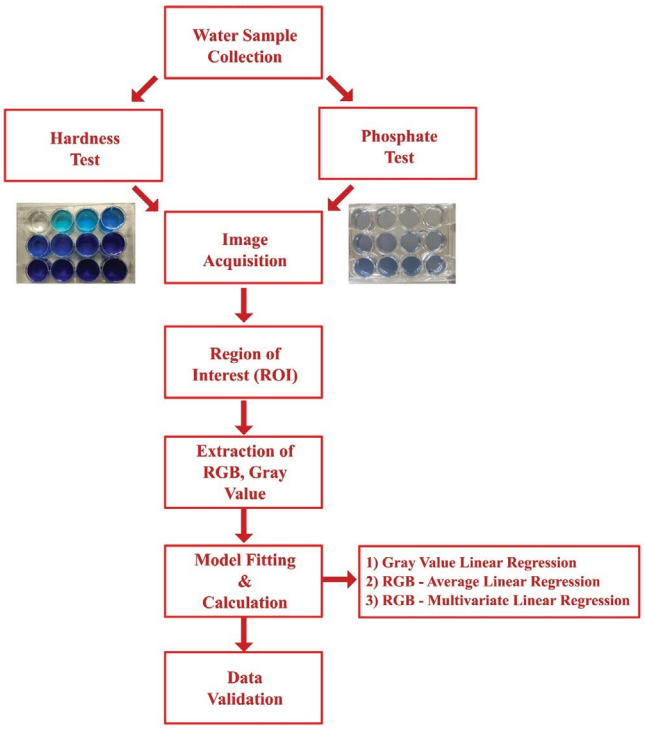

Fig. 1. Steps involved in the eutrophication analysis method reported in this study.

180, 200, and 250 mg/L and 20–100, 150, 200, and 250 μg/L, respectively. The images captured were stored and ROIs were cropped and stored. The gray intensity and RGB values of these images were further modeled with Eqs. (1) and (2).

Fig. 2 shows the linear models fitted for TH and TP data. The data obtained fit with the linear trend with a good precision. The regression coefficient and other statistical values obtained for TH and TP data fits are shown in Table 4. The modified R^2 values are 0.9932 and 0.9953, which showed that the fits were indeed accurate and acceptable. Also the root-mean-square error (RMSE) values show that there was a negligible error. The Eqs. (8) and (9) are used to determine the TH and TP values from gray intensity values. These equations were further used to analyze the unknown concentration of samples collected from various water bodies.

$$\mathrm{TH} = \frac{157 - I_{\mathrm{gray}}}{0.25} \tag{8}$$

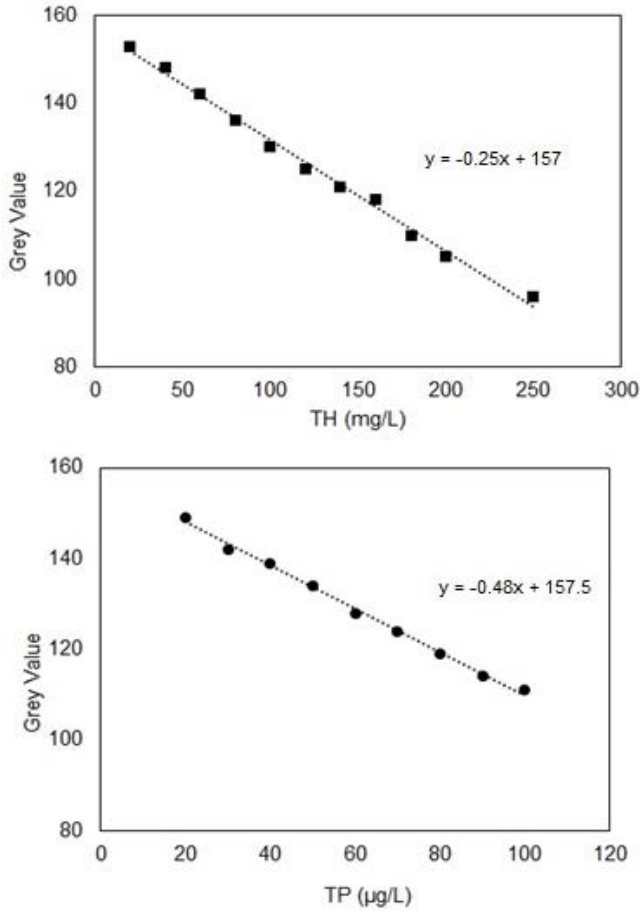

Fig. 2. Linear trend of gray values obtained for different TH and TP concentrations.

Table 4
Statistical parameters of gray value and RGB models

Equation	R^2	Adjusted R^2	RMSE
8	0.9939	0.9932	1.492
9	0.9959	0.9953	0.896
10	0.9866	0.9852	1.826
11	0.9669	0.9622	2.300

$$\mathrm{TP} = \frac{157.5 - I_{\mathrm{gray}}}{0.48} \tag{9}$$

Similarly, with the RGB data obtained using ROI images, I_{avg} values were determined and modeled using Eqs. (4) and (5).

Fig. 3 shows the linear trend of the data for both TH and TP experiments. The modified regression coefficients for these two models were 0.9852 and 0.9622, respectively, and it suggests that the model fits well with the experimental data. These values are slightly lower than the regression coefficients obtained for gray value model. This suggests that Eqs. (8) and (9) are more suitable than Eqs. (10) and (11). The RMSE values are also slightly higher (1.826 and 2.3) than the values obtained for Eqs. (8) and (9).

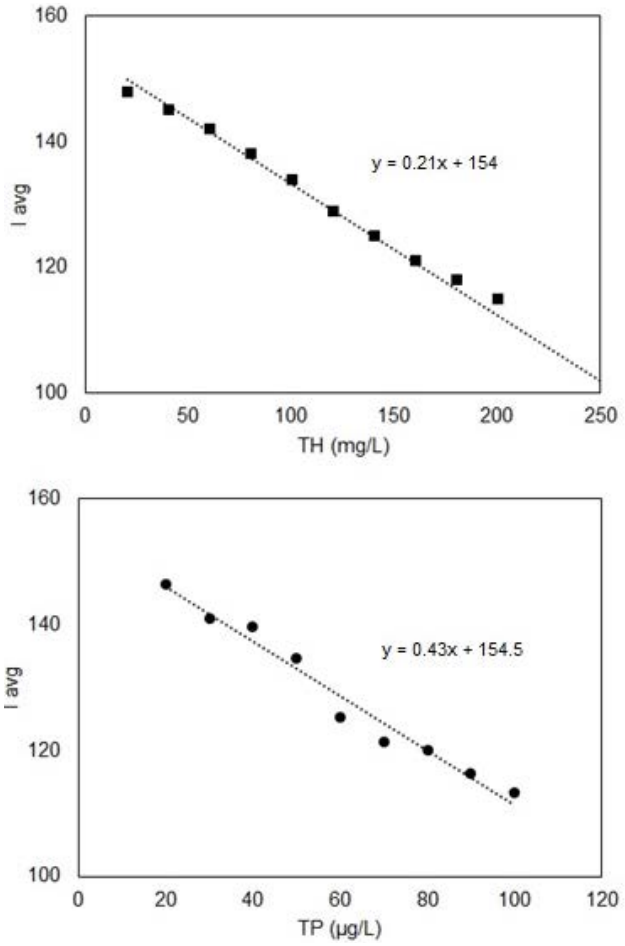

Fig. 3. Linear trend of average color intensity obtained for various TH and TP concentrations.

$$\mathrm{TH} = \frac{154 - I_{\mathrm{avg}}}{0.21} \tag{10}$$

$$\mathrm{TP} = \frac{154.5 - I_{\mathrm{avg}}}{0.43} \tag{11}$$

The RGB data were also analyzed using multivariate regression method to determine the polynomial equation used to calculate TH and TP concentration values. From the experimental data Eqs. (12) and (13) were derived.

$$\mathrm{TH} = 362.3 + 0.72I_R - 2.82I_G - 0.22I_B \tag{12}$$

$$\mathrm{TP} = 359.13 + 0.36I_R - 2.41I_G - 0.25I_B \tag{13}$$

The regression coefficient values obtained are 0.9802 and 0.9843, respectively.

3.2. Analysis of TH and TP of samples

The TH values obtained for five samples using four different methods are shown in Fig. 4. It is clearly interpreted from the figure that M2 and M3 determined the concentration values almost with the same precision as M1 which is considered the standard analytical method to determine the water quality parameters. M4, which is a multivariate regression analysis method predicted the concentration values slightly higher or lower to the actual values. This shows that M4 is not suitable for predicting the TH of water samples. The model derived using gray intensity values (M2) can be suitable for predicting the TH with less error (<1%). Also it is evident that S4 has very high TH value. Similarly, for TP analysis, S4 has high TP. M2 and M3 have high accuracy with standard analytical method (M1). The TP values of various samples using different methods are shown in Fig. 5

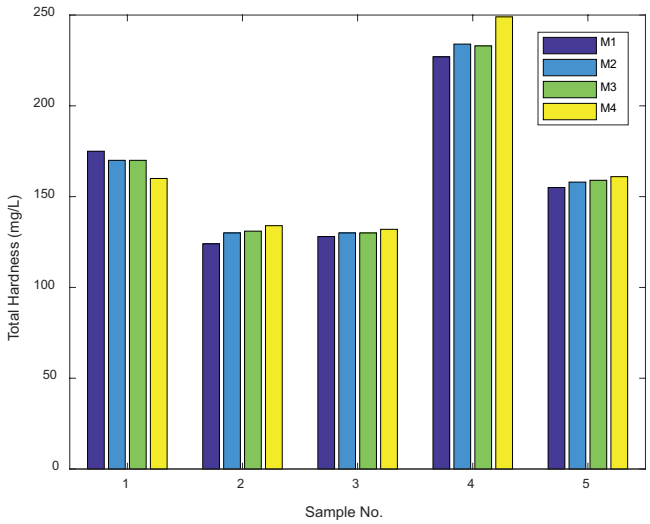

Fig. 4. Total hardness values obtained for five samples: comparative analysis of four different methods.

3.3. Analysis of eutrophication

Eutrophication level of water samples were determined by hardness and phosphorus concentrations. The standards

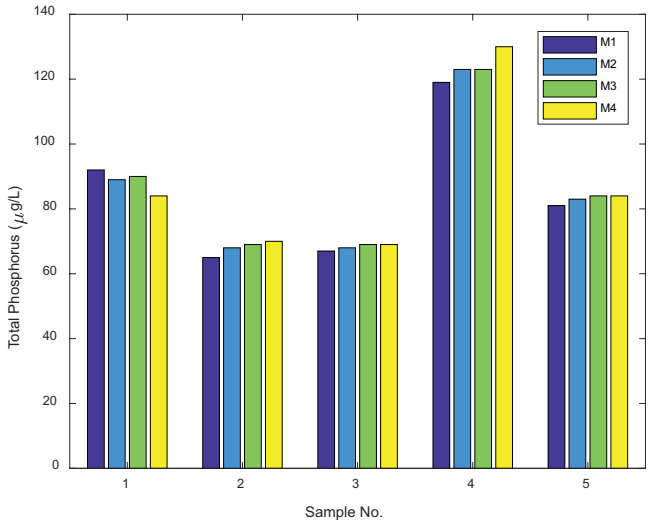

Fig. 5. Total phosphorus values obtained for five water samples using four different methods.

used to determine this is given in Table 3. The eutrophication levels of five water samples are mentioned in Table 5.

All five water bodies considered in this study were polluted with nutrient levels of higher degree. Water hardness of Thiruporur temple pond (S4) was very high and the degree of hardness is "very hard," also it has hypereutrophic status. This can be attributed to the poor maintenance of temple pond. However, the pond was surrounded by a busy market area which has higher degree of organic solid wastes just thrown away on the streets which during rainy season, were eroded into the temple pond. This increases the organic phosphates available in the pond water. Hundreds of people use this pond to take "holydip" every day. This in further contributes to the pollution of pond water. Visual examination of the pond water shows higher concentration of chlorophyll which another important parameter is showing higher eutrophication level. Apart from this, Kalavakkam lake and Thaiyur stream are also having a significant concentration of TP and TH. These water bodies are generally surrounded by agricultural fields and barren lands and roads, respectively. The higher degree of nutrient erosion from agricultural fields and barren lands contributes to the accumulation of nutrients in water bodies. Visual examination of these water bodies show that they are moderately greenish and aggregation of macroalgae could be seen in certain parts of these water bodies.

The results show that this method would be more suitable to monitor hardness and eutrophication of territorial water bodies by small group of people with limited skills. This also helps in continuous monitoring of water quality parameters and precipitating the data in a centralized cloud network which can be analyzed by respective scientist and officials. A simple automation can be done to regularize the monitoring process. An important advantage in this study is that the requirement of samples and reagents are considerably less.

The general existing procedure to measure hardness and concentration of other ions involve titrations, gas chromatograph–mass spectrometry (GC-MS) and flame atomic absorption spectrometry (FAAS). The cost of GC-MS [22] and FAAS [23] equipment is relatively high that small regional testing laboratories cannot afford them, whereas titrimetric method required the samples to be collected and preserved till the laboratory experiments were carried out. The computer vision-based analysis method has various advantages over the aforementioned methods. In this method, multiple number of samples can be analyzed at the same time. This method is faster than other existing methods. This method is also cheaper than the existing methods [24]. In this method, the cost of measurement for each sample is less than $1. Besides, the requirement of samples and reagents is in microliter scale. This method also predicts the parameters accurately compared with some methods, which predict the range of values.

Table 5
Eutrophication level of five water bodies considered in this study

Samples	Total hardness (mg/L)	Total phosphorus (μg/L)	Eutrophication level
S1	175	92	Eutrophic
S2	124	65	Eutrophic
S3	128	67	Eutrophic
S4	227	119	Hypereutrophic
S5	155	81	Eutrophic

4. Conclusions

Rapid and reliable analysis of water quality parameters has become the need of the day. Increasing water pollution became a great threat to the availability of pure water to the communities. This method proves to be highly suitable for a rapid "in situ" measurement of hardness and eutrophication level of water bodies. This method can be designed as a mobile or computer application which will make this even easier to analyze water quality by everyone without need of high skilled people.

References

[1] W. Zhang, I.C. Lou, Y. Kong, W.K. Ung, K.M. Mok, Eutrophication analysis and principle component regression for two subtropical storage reservoirs in Macau, Desal. Wat. Treat., 51 (2013) 7331–7340.
[2] A.Z. Stolarska, I. Zbicinski, M. Imbierowicz, J. Skrzypski, Waterpraxis as a tool supporting protection of water in the Sulejow Reservoir, Desal. Wat. Treat., 51 (2013) 4194–4206.
[3] S. Wang, T. Wang, L. Zhao, R. Li, Spatial distribution characteristics of phosphorus in the overlying water, interstitial and sediment of Lihu Lake, China, Desal. Wat. Treat., 65 (2017) 252–258.
[4] J. Dabrowska, K. Lejcus, M. Kusnierz, A. Czamara, J. Kaminska, I. Lejcus, Phosphate dynamics in the drinking water catchment area of the Dobromierz Reservoir, Desal. Wat. Treat., 57 (2016) 25600–25609.
[5] X. Ma, Y. Li, B. Li, W. Han, D. Liu, X. Liu, Evaluation of nitrogen and phosphorus loads from agricultural nonpoint source in relation to water quality in Three Gorges Reservoir Area, China, Desal. Wat. Treat., 57 (2016) 20985–21002.
[6] N. Yousefi, A. Fatehizedeh, K. Ghadiri, N. Mirzaei, S.D. Ashrafi, A.H. Mahvi, Application of nanofilter in removal of phosphate, fluoride and nitrite from groundwater, Desal. Wat. Treat., 57 (2016) 11782–11788.
[7] M. Zamparas, Y. Deligiannakis, I. Zacharias, Phosphate adsorption from natural waters and evaluation of sediment capping using modified clays, Desal. Wat. Treat., 51 (2013) 2895–2902.
[8] J. Artiola, I.L. Pepper, M.L. Brusseau, Environmental Monitoring and Characterization, Elsevier Science and Technology Books, USA, 2004.
[9] G.B. Wiersma, Environmental Monitoring, CRC Press, Boca Raton, 2004.
[10] B. Mitchell, Resource and Environmental Management, 2nd ed., Pearson Education Limited, Harlow, 2002.
[11] S. Weston, An Overview of Environmental Monitoring and Its Significance in Resource and Environmental Management, School of Resource and Environmental Studies, Dalhousie University, 2011.
[12] W. Giger, Hydrophilic and amphiphilic water pollutants: using advanced analytical methods for classic and emerging contaminants, Anal. Bioanal. Chem., 393 (2009) 37–44.
[13] M.-C. Hennion, P. Scribe, Chapter 2 Sample handling strategies for the analysis of organic compounds from environmental water samples, Techn. Instrum. Anal. Chem., 13 (1993) 23–77.
[14] M. Farré, L. Kantiani, M. Petrovic, S. Pérez, D. Barceló, Achievements and future trends in the analysis of emerging organic contaminants in environmental samples by mass spectrometry and bioanalytical techniques, J. Chromatogr., A, 1259 (2012) 86–99.

[15] N. Dujakovic, S. Grujic, M. Radisic, T. Vasiljevic, M. Lausevic, Determination of pesticides in surface and ground waters by liquid chromatography-electrospray-tandem mass spectrometry, Anal. Chim. Acta, 678 (2010) 63–72.
[16] E.E. Pissaloux, R. Velázquez, F. Maingreaud, A new framework for cognitive mobility of visually impaired users in using tactile device, IEEE Trans. Hum.-Mach. Syst., 47 (2017) 1040–1051.
[17] M. Heimberger, J. Horgan, C. Hughes, J. McDonald, S. Yogamani, Computer vision in automated parking systems: design, implementation and challenges, Image Vision Comput., 68 (2017) 88–101.
[18] J. Murphy, J.P. Riley, A modified single solution method for the determination of phosphate in natural waters, Anal. Chim. Acta, 27 (1962) 31–36.
[19] Standard Methods for the Examination of Water and Wastewater, APHA, AWWA and WEF, 21st ed. 2005.
[20] Standard Methods for the Examination of Water and Wastewater; APHA, AWWA and WEF, 20th ed., 2000.
[21] X. Yang, X. Wu, H. Hao, Z. He, Mechanisms and assessment of water eutrophication, J. Zhejiang Univ. Sci. B, 9 (2008) 197–209.
[22] D. Tsikas, K. Chobanyan-Jurgens, Quantification of carbonate by gas chromatography–mass spectrometry, Anal. Chem., 82 (2010) 7897–7905.
[23] T.V. Ramakrishna, J.W. Robinson, P.W. West, The determination of calcium and magnesium by atomic absorption spectroscopy, Anal. Chim. Acta, 36 (1966) 57–64.
[24] D. Damasceno, T.G. Toledo, A.S. Soares, S.B. Oliveira, A.E. Oliveira, CompVis: a novel method for drinking water alkalinity and total hardness analyses, Anal. Methods, 43 (2016) 7832–7836.