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Journal:	<i>Analyst</i>
Manuscript ID	AN-ART-12-2022-002086.R2
Article Type:	Paper
Date Submitted by the Author:	16-Mar-2023
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A low-cost automated titration system for colorimetric endpoint detection

Naga P. D. Boppana^a, Robyn Snow^a, Paul S. Simone^{a, b}, Gary L. Emmert^{a, b}, and Michael A. Brown^{a, b*}

An auto titrator system was developed to accurately and precisely detect colorimetric endpoints for spectrochemical titrations. This system was constructed using inexpensive components such as a Raspberry Pi® single-board computer, 3D-printed components, and a commercially available spectral sensor. The auto titrator was evaluated by performing a standard method for determination of water hardness. Regardless of analyst experience, the auto titrator performed better than the traditional titration approach that involves manual dosing of titrant and visual detection of the endpoint. Inter-day, intra-day, inter-instrumental, and intra-instrumental validation studies were performed to establish the accuracy and precision of endpoint detection. The auto titrator eliminates the subjective bias in color perception and produces accurate and precise endpoint results.

Keywords: Automation, Auto titrator, Colorimetric end-point detection, Raspberry Pi®, 3D-printing, Machine learning

Introduction

Titration is an absolute analytical technique commonly used for the determination of analyte concentration^{1,2}. Reliable delivery of titrant and endpoint determination are crucial for obtaining accurate and precise results. Traditionally, burets have been used for manual dosing of titrant during titrimetric analyses. The performance of this approach relies heavily upon the skill and effort of the analyst. Several potentiometric^{3,4}, conductometric^{5,6}, amperometric^{7,8}, and visual^{9–11} titration methods have been used to determine endpoints. Visual detection of an endpoint typically involves the use of a chemical indicator, which changes color at the endpoint. There are challenges associated with visual endpoint detection, such as when analysts determine different endpoints for the same standard which leads to high variability in test results. Also, some visual indicators lack a distinct color change making endpoint determination more difficult¹⁰. Furthermore, some indicators may produce an intermediate color prior to the “true” endpoint, this is referred to as dichroism. For example, bromocresol green exhibits a green color before changing from yellow to blue^{1,2}.

The majority of endpoint detection methods have been automated except visual methods where automated methods are limited^{12–15}. The use of spectrophotometer is a viable option for detecting color endpoints through absorbance measurement^{16,17}. Despite its high accuracy and relatively low detection limits, this technique is considered expensive and cumbersome. In recent years, Digital Image colorimetry (DIC)

has become increasingly popular for detecting color changes in chemical analysis^{18,19}. However, this technique is highly sensitive to lighting conditions and camera settings, which can result in measurement inaccuracies. Furthermore, the requirement for specialized equipment, including cameras and software, can increase the cost of digital colorimetry. Commercially available photometric titrators are relatively expensive for small and rural drinking water treatment plants (WTPs). The primary goal of this research was to develop a low-cost automated titration system that can deliver accurate and precise amounts of titrant and automate visual endpoint detection.

The proposed auto titrator was evaluated for performing water hardness titrations for finished drinking water and raw water. At drinking WTPs, total hardness titrations are performed each day to assess water quality. Water hardness is mainly due to the presence of calcium and magnesium salts and is reported as mg L⁻¹ of calcium carbonate (CaCO₃). The standard method for total hardness determination is based on complexometric titration and visual detection of color change at the endpoint^{10,11,20}. The use of a combination Ion Selective Electrode (ISE) is an option for the determination of total hardness²¹. However, the ISE method requires maintenance of the electrode and the presence of other inorganic ions in the water can affect the results. Furthermore, electrode fouling can compromise the accuracy of the method. Atomic absorption spectroscopy, while not a traditional method, can be utilized for determining total hardness²², though this method requires expensive instrumentation and trained personnel to operate and maintain the instrumentation making it less attractive for most drinking WTPs.

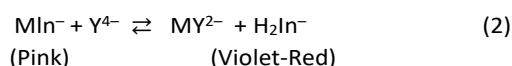
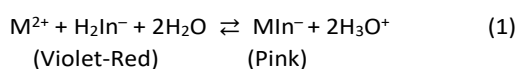
The standard titration method involves buffering a sample to pH 10.3 followed by addition a complexometric indicator (calmagite) followed by titration with standardized ethylene diamine tetraacetic acid (EDTA) titrant^{10,11,20}. The endpoint is reached when the Ca²⁺ and Mg²⁺ ions are fully displaced from

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the calmagite indicator by EDTA leading to a color change from pink to a violet-red color. Prior to the addition of EDTA, the Ca^{2+} and Mg^{2+} ions in the sample bind to the calmagite indicator producing a pink color as shown in Equation 1. EDTA is a stronger complexing agent than calmagite, so the EDTA displaces the metal ions from the indicator as shown in Equation 2 allowing the indicator to turn violet at the endpoint. The main issue with this approach is that different analysts have different sensitivities/perception to color change and differences in laboratory lighting may lead to variations in endpoint detection.



In this paper, a low-cost, automated titration system comprised of 3D-printed parts, stepper motors, a Raspberry Pi®, open-source Python programming for control and user interface, and other commercially available components was developed. With the proposed system, performing titrations will be as simple as a single click of a button. The cost of the developed system is approximately one third of other commercially available systems. Validation studies were conducted using the auto titrator to perform water hardness titrations at two drinking WTPs in Lebanon, TN and Woodruff, SC.

Experimental

Materials

The Raspberry Pi 3 B+® and a seven-inch capacitive touchscreen (LCD-13733) were purchased from Raspberry Pi® Foundation, UK. The AMIS-30543 (#2970) bipolar stepper drivers were purchased from Pololu (Las Vegas, NV, USA). The NEMA 17 1:5 gear ratio bipolar stepper motors (17HS15-1684S-PG5) were purchased from Stepper On-line, China. A 10 cm linear potentiometer, 16-bit analog to digital converter (ADS1115), and two switching mode power supplies (SMPS) (LS25-12 and RS15-5) were purchased from Digi-Key, USA. The linear bearings (63255K45), guide rod (1335T28), lead screw (1078N28) and nut (90591A161) for building syringe pumps were purchased from McMaster-Carr, USA. The SGE brand 5 mL gas tight glass syringes were purchased from TRAJAN (Austin, TX, USA). The commercially available spectral sensor board, AS7262, was purchased from SparkFun Electronics (Niwot, CO, USA).

Chemicals and Reagents

All reagents and standards were prepared using double distilled, deionized water with a resistivity >18.2 MΩ-cm and total organic carbon (TOC) of ≤10 μg L⁻¹ produced by a FI Strem III double distillation system (LabStrong, Dubuque, IA, USA) in series with a Barnstead E-Pure water purification system (Thermo Fisher Scientific, Waltham, MA, USA). This water is referred to as “reagent water” from this point forward. All chemicals were reagent grade or ACS certified grade except the

calmagite which was indicator grade. Calmagite and sodium carbonate were purchased from Acros Organics (New Jersey, USA). All other chemicals and reagents were purchased from Fisher Scientific.

The hardness stock standard solution was prepared by dissolving 0.5008 g of CaCO₃ (dried at 120 °C for two hours) into a 500-mL beaker containing 250 mL reagent water then 6 M hydrochloric acid (HCl) was added slowly until all the CaCO₃ was dissolved. The solution was heated to expel all the CO₂ and the pH was adjusted to approximately 5.0 with a 9 M ammonia solution (NH₃). This solution was diluted to a final volume of 500.0 mL using reagent water in a volumetric flask to give a concentration of 1016 mg L⁻¹ as CaCO₃.

A 0.01 M EDTA solution was prepared by dissolving approximately 1.862 g of EDTA disodium salt, dihydrate into 500 mL of reagent water and standardized with a standard calcium solution. Calmagite indicator solution (0.1% w/v) was prepared by diluting 0.1 g of solid calmagite in 100.0 mL of reagent water. An ammonia buffer (pH 10.3) was prepared by dissolving 1.179 g of EDTA disodium salt, dihydrate and 0.780 g magnesium sulfate heptahydrate in 100.0 mL of reagent water. Then, 16.9 g ammonium chloride (NH₄Cl) and 143 mL of concentrated ammonium hydroxide (NH₄OH) were added to the solution and diluted to 250.0 mL with reagent water. The hardness test solutions were prepared by diluting the stock solutions appropriately.

Development of automated titration system for color endpoint detection

The main components of the auto titrator are: (1) the titrant dosing system, (2) the spectrochemical detector, and (3) the control system and user interface.

Titration Dosing System: The titrant dosing system is based on a 3D-printed stepper motor syringe pump that was used to deliver titrant accurately and precisely in previous research^{23,24}. A 5-mL gas-tight syringe was used for the syringe pump and can deliver 100 μL of a titrant with 2% precision. The syringe pump consists of a NEMA-17 1:5 gear ratio bipolar stepper motor and an AMIS-30543 micro stepping bipolar stepper motor driver. A Raspberry Pi 3 B+® was used to generate the number of square pulses necessary to deliver precise quantities of the titrant. The absolute position of the syringe plunger was monitored by a plunger monitoring system. This system ensures the plunger is within the physical limits of the syringe barrel and provides feedback to determine the volume needed to refill or empty the syringe. A 10-cm linear potentiometer coupled with an ADS1115 digital converter was used to determine the plunger position.

Spectrochemical Detector: The spectrochemical detector consists of a spectral sensor board (AS7262) with six optical channels for color detection and 3D printed enclosure. The AS7262 features a compact design and integrated broad-spectrum LED as a light source. Each optical channel of the AS7262 board has an interference filter deposited on the complementary metal-oxide semiconductor silicon capable of detecting visible wavelengths with peak sensitivities at 450 nm,

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500 nm, 550 nm, 570 nm, 600 nm, and 650 nm. Each spectral channel has an effective bandwidth of 40 nm full width at half height²⁵. This sensor can detect wavelengths in the visible range from 430 nm to 670 nm making it highly versatile for a wide range of applications without the need to change the LED or detector. The photocurrent produced from each channel is digitized using an integrated 16-bit analog to digital converter. The hollow cylindrical part (Figure 1A) of the 3D-printed enclosure is specifically designed to hold a 30-mL beaker. The AS7262 board was installed in the square enclosure (Figure 1B) located behind the hollow cylinder. This enclosure has a 3D-printed cover with rubber gasket to protect against water as well as minimize the interference from external light. Two apertures were added to the hollow cylinder section: one to allow the light from the light emitting diode (LED) on the AS7262 board to illuminate the sample and the other one to allow the reflected light from the sample to be detected by the spectral sensor. The detector assembly was attached to the top plate of the aluminum enclosure that has an embedded magnetic stirrer (Figure 1C). The stirrer was constructed by 3D-printing a support vane to hold two small neodymium magnets at each edge that was placed on the shaft of a miniature 12V DC motor. The DC motor was positioned in the enclosure to align directly beneath the hollow cylinder (Figure 1A). The stirring speed was controlled using a pulse width modulation (PWM) controller board. The detector compartment is designed in such a way that ambient light has minimal effect on detector response. Also, the detector does not have to be immersed in the sample which reduces the risk of contamination and eliminates concerns about the compatibility of detector housing materials with the sample solution.

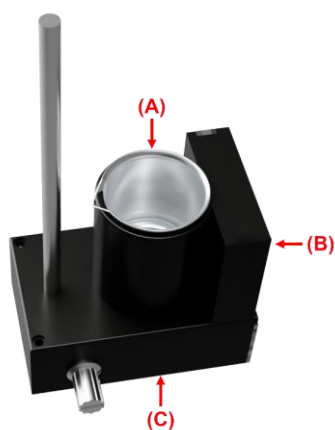


Figure 1. Top-down view of the 3D-printed spectrochemical cell holder with embedded magnetic stirrer. (A) Beaker holder, (B) Spectral sensor compartment, (C) Aluminium enclosure with magnetic stirrer.

Control System and user interface: A Raspberry Pi[®] was used for control, signal processing, and communication with the external hardware like stepper drivers and the spectral sensor board in conjunction with the open-source Python programming language. A Graphical User Interface (GUI) for the auto titrator was developed using Tkinter, a standard GUI package in Python. The developed GUI has two pages as shown in Figure 2.

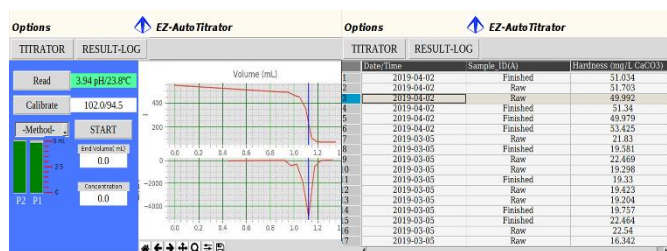


Figure 2. Graphical user interface developed for the auto titrator. The image on the left side shows the Titrator page and the right side shows the Result log page.

The Titrator page has options to report pH, temperature and select the type of titration to perform. It also displays the plot of real-time pH or light intensity versus volume, the associated first derivative plot, and final hardness result. The Titrator page allows the user to change titration parameters such as the titrant concentration, sample volume, end pH, and pre-dose volume. The Results log page saves the hardness results with a timestamp. A capacitive touchscreen was used to provide user interaction with the GUI and display results.

Development of color prediction machine learning model

Unlike most pH titrations, spectrochemical titrations do not have a specific “color” value where a titration can be stopped unless a titrator system is programmed to detect the color change and stop the titration. One of the primary goals of this research was to develop a color prediction model that can distinguish the starting and end-point color by using a simple machine learning algorithm. Scikit-Learn is a powerful yet simple to use open-source machine learning Python library that incorporates classification, regression and clustering algorithms was used for modeling^{26,27}. The K-nearest neighbor (KNN) classification algorithm²⁸ was used to develop the model for color determination through the AS7262 spectral sensor input. Several analyte samples were prepared by combining different amounts of analyte and reagents to generate the initial color. The samples were analyzed individually to record the data from the six spectral channels of the AS7262. The samples were then titrated until the desired color change was achieved and the data was recorded from the spectral sensor. The collected data was randomly divided into a training data set and a test data set in the ratio of 80/20, a standard approach in machine learning. The KNN model was then trained on the training data set and the test data set was used to evaluate the model. The developed KNN model was integrated into the GUI program. When required, responses from all six spectral channels of the AS7262 are collected and supplied to the model. The model then analyzes this input data and produces a prediction for the color.

Procedure for total hardness using the auto titrator

For the determination of total hardness, a 15 mL volume of drinking water sample was transferred using a volumetric pipet into a 30-mL beaker. Three drops of calmagite indicator and three drops of ammonia buffer (pH 10.3) were added to the sample. The solution was then titrated with standardized 0.01 M EDTA solution until the sample color changed from pink to violet with a slight red tinge as determined by the KNN color

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prediction model. The volume of the EDTA solution determined from the minimum of first derivative curve was selected as the endpoint volume. The Hardness of the sample was calculated²⁰ as shown in Equation 3.

$$\text{Hardness, mg L}^{-1} \text{ CaCO}_3 = V_y \times M \times 100,000 / \text{Sample Volume (3)}$$

Where V_y is the volume (mL) of standardized EDTA used to titrate, the sample calculated from first derivative curve and M is the molarity of the standardized acid. A conversion factor of 100,000 with units of mg mol^{-1} converts the sum of moles per liter of calcium and magnesium to $\text{mg L}^{-1} \text{ CaCO}_3$.

Validation Studies

Intra-instrumental and inter-instrumental accuracy and precision studies were performed to validate the results of the hardness titrations for the auto titrator. The accuracy and precision of each set of titrations were estimated by analyzing a hardness standard solution (50.1 mg L^{-1} of CaCO_3) seven times per study. The analysis of variance (ANOVA) at a 0.05 significance level was performed to test the null hypothesis that means from all test groups are equal^{29,30}. Moreover, accuracy and precision of the auto titrator was assessed across a range of hardness concentrations to evaluate the impact upon titration results. The accuracy was estimated as mean percent recovery as per the USEPA guidelines^{31–33} and the precision was calculated as percent relative standard deviation (%RSD) of seven replicates^{2,34}.

Real World Testing

The auto titrator was tested at Lebanon, TN and Woodruff, SC WTPs. The hardness value of finished and raw water was determined by the auto titrator then compared with the manual titrations for over four months at Lebanon, TN WTP. At the Woodruff, TN WTP, the auto titrator was compared with manual titrations for two days for finished, floc-3 (water after flocculation) and raw water samples. A 50 mL sample volume was used for manual hardness titrations while the auto titrator used 15 mL of sample. Due to time constraints for the WTP operators, replicate measurements for individual time points were not able to be performed.

Results and Discussion

Evaluation of color prediction model

The test data set was tested on the trained KNN model. The weighted averages of accuracy, precision, recall, and F1-score were calculated^{28,35}. Based on these evaluation parameters, the KNN model was shown to have acceptable performance with accuracy, precision, recall, and F1 score all equal to 1.

Operation of auto titrator for performing hardness titrations

When a hardness titration has been selected, this begins the decision tree shown in Figure 3. First, the spectral sensor is set to read the intensity of reflected light at 650 nm continuously as the reflectance of the calmagite best overlaps with this wavelength. The titrator predicts the color of the sample using KNN color prediction model. If the color of the sample is not

the endpoint color, then the titrator adds a relatively large amount of titrant called a predose to speed up the titration and waits for 15 secs to allow the titrant and sample to adequately mix. The auto titrator then measures the light intensity from all the channels and predicts the color of the sample again. If the color is not the endpoint color, the auto titrator adds smaller doses of titrant and this process will be repeated until there is a color change as determined by the machine learning model. At the end of the titration, the endpoint volume is calculated based on first derivative plot generated from volume versus the intensity of light from the 650 nm optical channel.

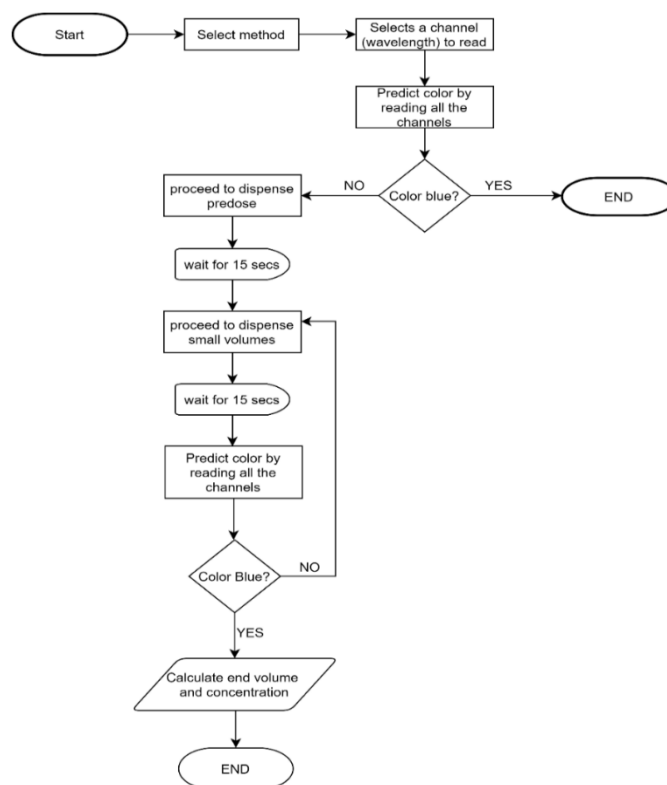


Figure 3. Flow chart which outlines the detection of color change at the endpoint for the auto titrator system. For hardness, the color changes from pink to violet with a red tinge.

Results from Validation Studies

Validation studies were performed to evaluate the accuracy and precision of the auto titrator for performing automated hardness titrimetric analyses. The results of these validation studies are detailed in Table 1. For the intra-instrumental evaluation, a 50.1 mg L^{-1} hardness standard solution was analyzed by two different auto titrators. The mean of the hardness results for the two titrators was exactly the same (49.3 mg L^{-1}) indicating acceptable precision of electronics particularly the AS7262 spectral sensor and the machine learning model used to detect the endpoint color.

Inter-day accuracy and precision were evaluated by comparing the hardness results determined over three days using the same auto titrator. The means ranged from 48.6 to 49.3 mg L^{-1} . The results from ANOVA tests suggest that the means were not statistically different. An intra-day evaluation of accuracy and

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precision was performed by comparing the hardness results from the same auto titrator at three different times within a single day. The means of three trials ranged from 49.3 to 50 mg L⁻¹ which are not statistically different. The majority of the trials in validation tests shown in Table 1 and Table 2 have precision of 0.0% which is unexpected and counterintuitive for typical instrumental analysis. Normally, some variation is expected due to the random variations in the analytical signal. The uniformity of the precision values is due to the operation of the auto titrator. After the predose, the titrant is added in increments of 50 µL when titration is close to the endpoint. This increment is equivalent to ~3 mg L⁻¹ CaCO₃ of hardness. In addition, this also means that the random “noise” from the syringe pump and spectral sensor is less than 3 mg L⁻¹, indicating the hardness detection limit is likely lower. The auto titrator cannot distinguish a change in hardness below 3 mg L⁻¹ and at a WTP this inability to distinguish below 3 mg L⁻¹ is considered to be a negligible error in routine WTP operation. Overall, the auto titrator has an average recovery of 98.5% with an %RSD of 0.8% (49.3 ± 0.4 mg L⁻¹ CaCO₃).

Table 1: Validation results for total hardness using the auto titrator.

Test (n = 7)		True Value (mg L ⁻¹)	Measured Value (mg L ⁻¹)	Accuracy (Precision)	Means Statistically Different? (p < 0.05)
Intra-instrumental	Auto Titrator-1	50.1	49.3	98.5% (0.0%)	NO
	Auto Titrator-2	50.1	49.3	98.5% (0.0%)	
Inter-day	Day-1	50.1	48.6	99.9% (3.1%)	NO
	Day-2	50.1	49.3	98.5% (0.0%)	
	Day-3	50.1	49.3	98.5% (0.0%)	
Intra-day	Iteration-1	50.1	50.0	99.9% (3.0%)	NO
	Iteration-2	50.1	49.3	98.5% (0.0%)	
	Iteration-3	50.1	49.3	98.5% (0.0%)	

Table 2 summarizes the accuracy and precision of hardness titrations over a range of hardness concentration values ranging from 10 to 200 mg L⁻¹. All the tested concentrations have acceptable recoveries ranging from 93.4 to 104.4% except for 10 mg L⁻¹ where the recovery was ~85%. At lower concentrations (around 10 mg L⁻¹), higher sample volumes (30 mL) might improve the accuracy of results.

Table 2. Total hardness concentration results from the auto titrator at different concentrations.

	Total Hardness Concentration (mg L ⁻¹ CaCO ₃)				
	Nominal	10.0	20.0	50.1	100.1
Mean (n=5)	8.5	18.7	48.6	96.9	209.1
Accuracy	84.9%	93.4%	97.1%	96.8%	104.4%
Precision	0.0%	0.0%	3.1%	0.0%	0.0%

A t-test was used to compare the auto titrator and manual hardness titrations are shown in Table 3. Both the methods have mean % recoveries close to 100% but the auto titrator is slightly better at 100.3% compared to the manual titrations at 102.6%. The t-test suggests the means are statistically different. These results are expected as manual titrations rely upon analyst ability to reliably detect the endpoint after the calmagite indicator color transition has occurred. This means an analyst will deliver more titrant than necessary, resulting in a mean % recovery greater than 100%. For the auto titrator, the high dosing accuracy in combination with detection of the endpoint by the AS7262 spectral sensor and a first derivative plot captures the transition between pink and violet with red tinge at the correct point in the titration more accurately and reproducibly.

Table 3: Comparison of total hardness results for the auto titrator and manual titration.

	Manual Titration	Auto Titrator
True Concentration (mg L ⁻¹)	50.1	50.1
Mean (n = 20)	51.4	50.2
Accuracy	102.6%	100.3%
Precision	2.0%	3.0%
t-test	Failed: means are statistically different	

Comparison of hardness results for the auto titrator and manual titration at Lebanon, TN WTP

Water hardness was determined using the auto titrator and manual method by a Lebanon WTP operator daily for both finished and raw water. The comparison of hardness results for the two methods are presented in Figure 4A and Figure 4B for raw and finished water, respectively. The average hardness was found to be 82.7 mg L⁻¹ in raw water and 81.7 mg L⁻¹ in finished water. The average difference (auto titrator – manual) between the two methods was found to be -1.2 ± 4.6 mg L⁻¹ CaCO₃ in raw and -0.6 ± 4.6 mg L⁻¹ CaCO₃ in finished water.

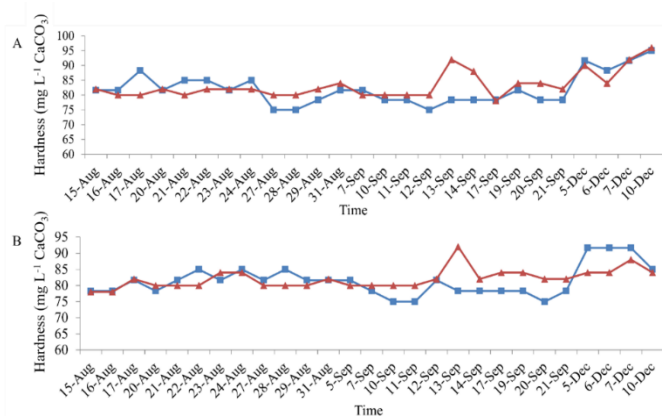


Figure 4: Total hardness results for (A) raw water and (B) finished water at Lebanon, TN water treatment plant determined by the auto titrator and manual titration method. The red line with triangle markers represents the manual titration results. The blue line with square markers represents the auto titrator results.

The Bland-Altman plot^{36,37} for raw water (Figure 5A) has difference scattered around the mean difference with no sign of a proportional difference. The finished water (Figure 5B) seems to have an apparent proportional error; however, the hardness range is relatively small, $\sim 75 - 85 \text{ mg/L CaCO}_3$ and concluding a proportional difference exists is difficult given that the range of hardness for all the other samples was similarly small.

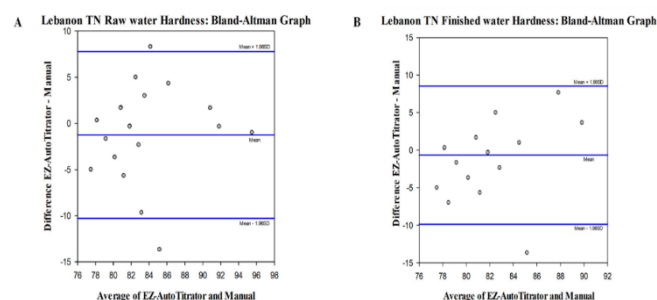


Figure 5: Bland-Altman plots for comparison of hardness results for (A) raw water and (B) finished water at Lebanon, TN water treatment plant determined by the auto titrator and manual titration method.

Comparison of hardness results for the auto titrator and manual titration at Woodruff, SC WTP

Total hardness results were compared between the auto titrator and those for the manual titration of raw (Figure 6A), floc-3 (water after flocculation) (Figure 6B) and finished water (Figure 6C) for two days. Measurements were made every two to three hours between 8 am and 5 pm each day. The average measured hardness was found to be around 28 mg L^{-1} in finished water and floc-3. The lowest average hardness (18 mg L^{-1}) was measured in raw water. The average difference was found to be $-2.9 \pm 1.7 \text{ mg L}^{-1} \text{ CaCO}_3$, $-2.6 \pm 1.5 \text{ mg L}^{-1} \text{ CaCO}_3$ and $-1.9 \pm 2.3 \text{ mg L}^{-1} \text{ CaCO}_3$ in raw, floc-3 and finished water respectively. The Bland-Altman plots for raw, floc-3, and finished water were shown in Figure 7 A, B, and C respectively.

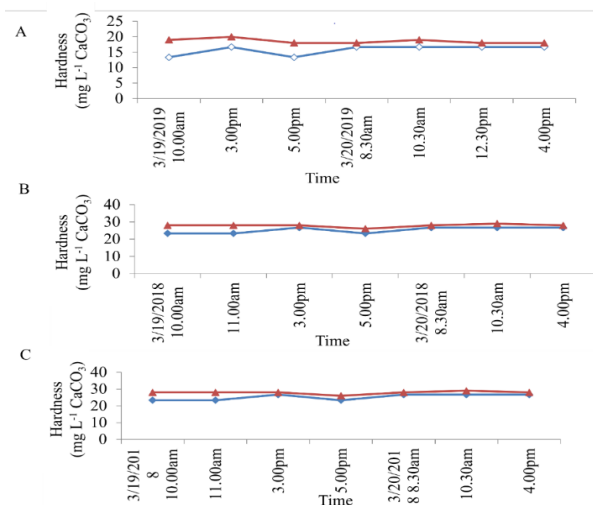


Figure 6: Total hardness results for (A) raw, (B) floc-3, and (C) finished water at Woodruff, SC water treatment plant determined by the auto titrator and manual titration method. The red line with triangle markers are the manual titration results. The blue line with square markers represents the auto titrator results.

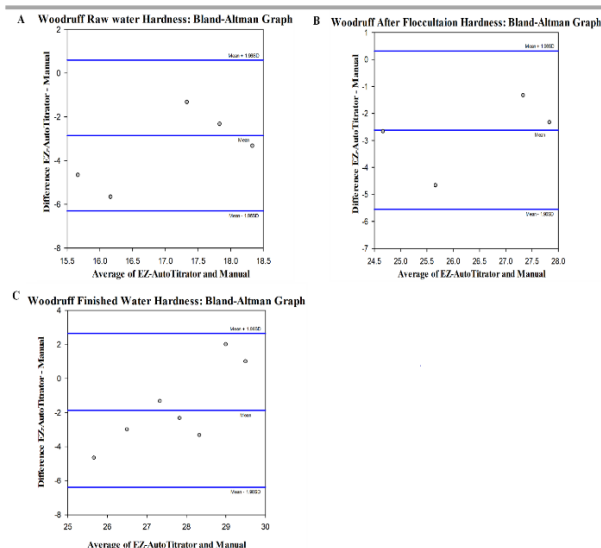


Figure 7: Bland-Altman plots for comparison of hardness results for (A) raw, (B) floc-3, and (C) finished water at Woodruff, SC water treatment plant determined by the auto titrator and manual titration method.

Conclusions

An automated titration system was developed using a Raspberry Pi® single board computer, 3D-printed components, and commercial-off-the-shelf components. A two-channel auto titrator was constructed for under \$1,000. A total hardness titration method was developed and rigorously tested demonstrating equivalent or better results to manual titrations. The auto titrator was successfully tested for determination of water hardness at Lebanon, TN WTP for over three months in raw and drinking water. A second on-site test was conducted at the Woodruff, SC WTP comparing the auto titrator to a manual titration for two days for raw, water after flocculation, and finished water. The analysis of Lebanon WTP water evaluated

the performance of the auto titrator at mid to higher hardness levels while the test performed at Woodruff WTP evaluated the performance of the titrator for lower hardness concentrations. Due to lack of replicate sample measurements, the uncertainty of the measurements from both these testing sites could not be assessed. Additionally, the auto titrator was certified for use as a standard method for measuring water hardness at Lebanon WTP by LabtronX Inc. a company specialized in quality assurance.

Author Contributions

N.P.D.B.: Conceptualization, Software, Formal Analysis, Investigation, Validation, Writing – original draft. R.S.: Investigation, Methodology, Writing – Review & editing. M.A.B.: Conceptualization, Funding acquisition, Visualization, Writing – review & editing. P.S.: Funding acquisition, Project administration, Resources, supervision, Writing – Review & editing. G.E.: Conceptualization, Formal Analysis, Methodology, Supervision, Funding acquisition, Writing – Review & editing.

Conflicts of interest

Gary L. Emmert, Paul S. Simone, and Michael A. Brown are part-time employees/owners of Foundation Instruments, Inc. The SBIR Phase II NSF Grant #1556127 awarded funds to Foundation Instruments, Inc. to develop products such as the auto titrator. The auto titrator is patent pending and will be commercially sold.

Acknowledgements

The authors are grateful to Foundation Instruments, Inc. for funding portions of this research and permission to use their 3D-Printing facility and machine shop. This material is based upon work supported by National Science Foundation under Grant No. 1556127.

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