

Real-Time Detection of Residual Free Chlorine and pH in Water Using a Microchannel Device

Sam Hwan Kim¹, Ju Chan Choi¹, June Kyoo Lee¹, and Seong Ho Kong^{2,+}

Abstract

A microfluidic device for real-time monitoring of residual free chlorine and pH in water based on optical absorption is proposed. The device consists of a serpentine micromixer for mixing samples with a reagent, and a photodiode and light emitting diode(LED) for the detection of light absorbance at specific wavelengths, determined for specific reagent combinations. Spectral analyses of the samples mixed with N, N'-diethyl-p-phenylenediamine(DPD) reagent for chlorine determination and bromothymol blue(BTB) for pH measurement are performed, and the wavelengths providing the most useful linear changes in absorbance with chlorine concentration and pH are determined and used to select the combination of LED and photodiode wavelengths for each analyte. In tests using standard solutions, the device is shown to give highly reproducible results, demonstrating the feasibility of the device for the inexpensive and continuous monitoring of water quality parameters with very low reagent consumption.

Keywords : Microchannel, Colorimetric Method, Absorbance, Mixing Index

1. INTRODUCTION

The supply of potable water in sufficient volumes has become one of the major challenges faced by modern society. Soaring populations in urban areas, a lack of infrastructure for supplying this population with drinking water in many countries, and global climate change have exacerbated this problem considerably. At the same time, standards for water quality are becoming more stringent, requiring the development of monitoring devices capable of rapid analysis. Many devices for water quality measurement based on electrical or optical methods have been developed and commercialized[1-4].

The water quality monitoring instruments available at present provide automated measurements and high sensitivity. Yet the devices are generally bulky and heavy, and incur high maintenance costs. Portable devices have also been developed but most of these devices require manual operation and do not provide real-time monitoring. Therefore, there is a need to improve on these weaknesses of both types of conventional devices.

Microfluidics systems have been developed for use in

many applications in a diverse range of fields, from electrochemical to deoxyribonucleic acid(DNA) detection and chemical synthesis[5-7]. This technology has the benefit of low sample and reagent consumption, fast processing and detection, and good bio and chemical compatibility.

In the course of this research, a microfluidics-based scheme for measuring water quality parameters of free chlorine and pH continuously in real-time was developed. The system uses optical sensors to monitor the quality of the water flowing through the microchannel of the device.

The resultant system has been shown to provide economical and efficient water quality monitoring by dramatically reducing the amount of reagent needed for analysis compared to conventional devices, resulting in much lower ongoing maintenance costs.

2. EXPERIMENTS

2.1 Microchannel design

In straight microchannels, the mixing of fluids is poor because of the low interfacial contact area between fluids, confining the mixing mechanism to diffusion within a low Reynolds number regime. In this study, a basic passive serpentine micromixer with a simple fabrication procedure

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was designed to promote the mixing efficiency of the sample water and reagent within the microchannel. The serpentine microchannel is embedded with periodic obstacles to increase chaotic advection by disturbing the fluid without adding complexity to device. Figure 1 shows a schematic view of the microchannel. The channel is 500 μm wide and 100 μm deep, and has square obstacles with a side length of 250 μm embedded at intervals of 650 μm . To ensure adequate mixing, the microchannel has a length of 10 cm.

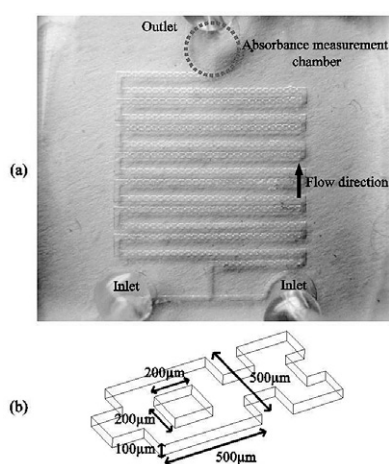


Fig. 1. (a) Fabricated microchannel and (b) schematic view of the microchannel.

2.2 Fabrication of microchannel

The microchannels were fabricated using a combination of silicon micromachining and soft lithography. The mold for the microchannel was prepared from a silicon wafer coated with AZ 9260 photoresist and baked at 110 °C on a hot plate for 180 secs. A patterned film mask was then placed on the photoresist-coated silicon wafer and exposed to ultraviolet light (365 nm) for 350 secs. After the development process, the wafer was etched by deep reactive ion etching and the remaining photoresist was removed using acetone and methanol. The channel mold was then cut into a square chip using a dicing machine. A pre mixed 10:1 volume ratio of polydimethylsiloxane (PDMS) elastomer and curing agent (Sylgard 184, Dow Corning Copr., USA) was subsequently cast on the channel mold and cured, after which the PDMS layer was separated from the mold and punched with holes for the inlet and outlet. Pyrex glass cut to the correct size was then bonded to the PDMS layer after surface treatment using the corona discharge from a Tesla coil. Pipette tips were fixed to the inlet and outlet holes using an

adhesive to connect the microchannel and the tubes linked to an external pump. These processes are depicted in Fig. 2.

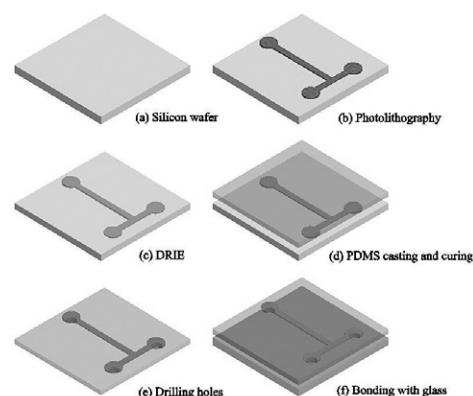


Fig. 2. Microchannel fabrication flow chart.

2.3 Preparation of samples and reagents

Korean standards for water quality stipulate a maximum residual free chlorine concentration of 4 mg/L and a pH range of 5.8 to 8.5. N,N 2-diethyl-p-phenylenediamine (DPD) is a sensitive reagent for free chlorine detection in this concentration range, and bromothymol blue (BTB) and litmus are suitable for pH detection. Calibration samples containing 0 mg/L - 10 mg/L free chlorine were prepared using a 14 % concentration of sodium hypochlorite (NaOCl) in deionized water. Then 0.25 g DPD powder was added to these samples, causing the solutions to turn pink. Using these chromatically reacted samples, spectrum analysis was carried out to determine the wavelength of the light emitting diode (LED) to be used in the microchannel cell and the required absorbance characteristics of the photodiode. Figure 3 shows the results of these spectral analyses as a function of chlorine concentration.

Standard pH solutions were prepared by mixing 100 mL

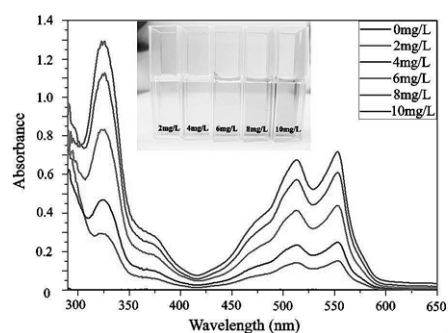


Fig. 3. Spectrum analyses of DPD reagent solution mixture with free chlorine sample solution.

deionized water solutions with BTB(0.25 %) and litmus reagent(4 g). Figures 4 and 5 show results of the spectral analyses and the images of the mixed solutions.

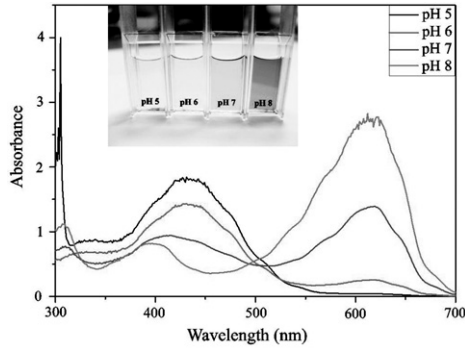


Fig. 4. Spectrum analyses of BTB reagent solution mixture with pH standard solution.

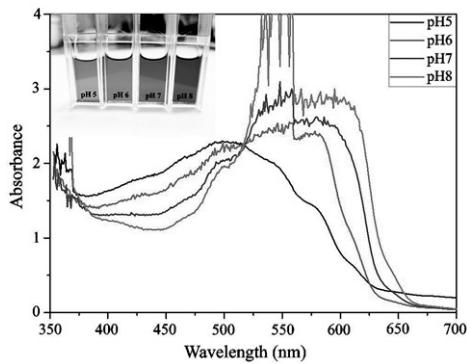


Fig. 5. Spectrum analyses of litmus reagent solution mixture with pH standard solution.

Based on the spectral analyses, the absorbance changes at the wavelengths corresponding to absorbance peaks were analyzed in order to optimize the wavelength of the light source used for each analyte.

The absorbance changes as a function of free chlorine concentration at three absorbance wavelengths are shown in Fig. 6. Although the absorbance change at 323 nm is the largest, this wavelength is in the ultraviolet range, to make optical measurements in this range requires complex, expensive devices. The absorbance changes at 515 and 553 nm are smaller but still usable. The wavelength of 515 nm, which corresponds to the emission of commercial green LEDs, was finally selected for the measurement of residual free chlorine.

The absorbance changes for standard pH solutions with BTB and litmus reagent are shown in Figs. 7 and 8. Two wavelengths were sorted for each case, and 455 nm(blue

LED) was selected for BTB based pH detection. The peaks at 612 nm for BTB and 607 nm for litmus displayed nonlinear absorbance changes and were thus unsuitable for our device.

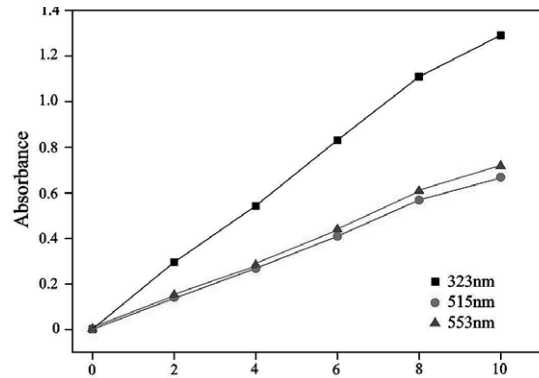


Fig. 6. Calibration lines for absorbance as a function of chlorine concentration.

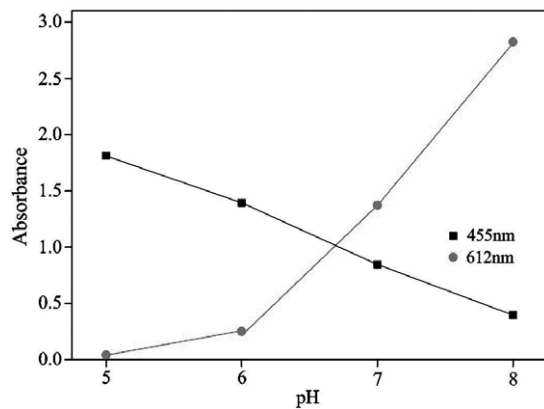


Fig. 7. Calibration lines for absorbance as a function of pH value in the case of BTB reagent.

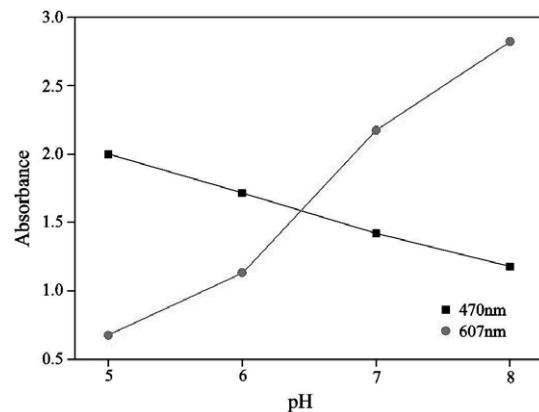


Fig. 8. Calibration lines for absorbance as a function of pH value in the case of litmus reagent.

2.4 Measurement setup

A schematic of the measurement setup is shown in Fig. 9. The fabricated microchannel was connected to an external pump via a silicon tube. An LED was fixed over the detection chamber and a photodiode was placed underneath the chamber and soldered to a printed circuit board. The LED was connected to a power supply, and a source meter was used to monitor the output signal of the photodiode.

Solution samples and reagents were injected continuously into the inlet and mixed by passing through the mixing microchannel. Chromatic reactions in the sample were then used to determine pH and free chlorine concentration based on the intensity of the transmitted light.

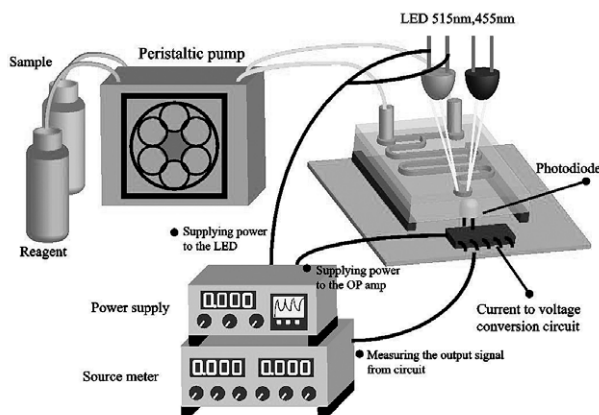


Fig. 9. Schematic view of the measurement setup.

3. RESULTS AND DISCUSSIONS

3.1 Measurements

The results of continuous free chlorine concentration detection using the microchannel device are shown in Fig. 10. The reproducibility of the measurements was tested by injecting the same concentration of chlorine solution into the device three times at 30 secs intervals, with deionized water injected into the device to purge the channel between each measurement. As the results show, the signal was stable during this reproducibility test. The same level of reproducibility was found for pH detection, as shown in Fig. 11. In the case of pH, the output voltage of the sensor is inversely proportional to pH because of the negative absorbance sensitivity.

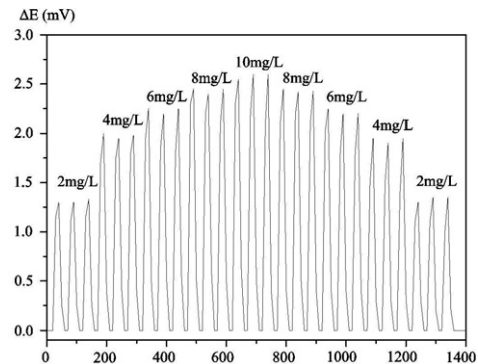


Fig. 10. Measurements for free chlorine concentration.

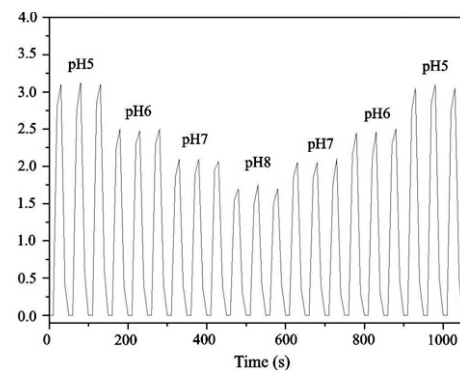


Fig. 11. Measurements for pH value.

3.2 Simple mixing index determination

To evaluate the performance of the micromixer quantitatively, a mixing index was derived. Conventionally, image processing software and image capturing devices have been used to analyze the mixing index of a microchannel. Such captured images are numerically analyzed using the color intensity of each pixel. Although this method can give accurate results, expensive equipment is required in order to apply this approach properly[8-10].

Therefore, a simple method for deriving the mixing index without an expensive experimental setup was developed. However, the degree of mixing of two solutions passing through a microchannel can be determined from the stability of the transmitted light intensity. That is, perfectly uniform mixing of two solutions should produce a highly stable signal equivalent to that of a single homogeneous solution, whereas poor mixing will result in modulation of the transmitted light intensity as transmission occurs through a solution composed of a variable ratios of the two component solutions. Hence, the stability of the detected absorption signal should be closely related to the mixing

index of the microchannel.

This approach was tested experimentally using a standard pH 8 solution and BTB. The solution is a uniform purple in the 100 % mixed condition. The mixing index was determined by referring to the mixing performance of a T mixer, which is known to provide minimal mixing. Under a constant flow rate, the mixing index is given by

$$\text{Mixing index} = \frac{I_{T\text{mixer}} - I_{\text{mixer}}}{I_{T\text{mixer}} - I_{\text{max}}} \quad (1)$$

where $I_{T\text{mixer}}$ is the photodiode current for mixing in a T mixer, I_{mixer} is that for the microchannel under test, and I_{max} is the theoretical current for perfect mixing. A mixing index close to 1 corresponds to good mixing while a value closer to 0 represents poor mixing performance.

Mixing index tests were conducted using the proposed method and various microchannel mixers. The results are shown in Fig. 12 and summarized in Table 1. The present mixing index results for a Tesla microchannel, T channel and modified T channel devices (flow rate, 50 $\mu\text{L}/\text{min}$; channel length 2 cm; channel width 200 μm ; channel depth 100 μm), are consistent with the reported values using image-based methods.

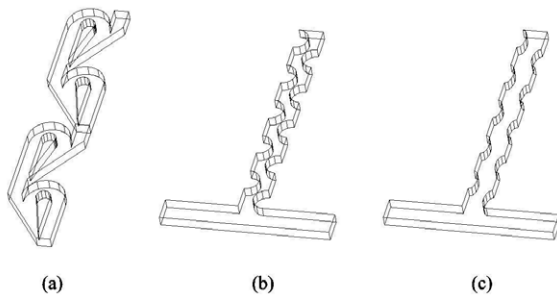


Fig. 12. Microchannel design: (a) modified Tesla structure[11], (b) modified T-channel 1, (c) modified T-channel 2.

Table 1. Results of the mixing index

Micro channel	Reported Mixing index	Measured Mixing index
(a)	0.88	0.85
(b)	-	0.31
(c)	-	0.13

4. CONCLUSIONS

A micro channel device for monitoring free chlorine concentration and pH in continuous flowing water was demonstrated. The measurement of the three water parameters is based on the light absorbance characteristics of the sample at specific wavelengths after thorough mixing of the sample with a reagent. The proposed device provides optimal mixing performance through a easily fabricated serpentine microchannel with obstructions. The light absorbance characteristics of the sample and reagent mixtures were determined through spectral analysis, which provided a basis for the selection of the light source(LED) and photodiode for detection. Real-time absorbance measurement of the reagent-mixed solutions was successfully performed using an extremely small volume of reagent and the results were demonstrated to be highly reproducible. Therefore the proposed method represents a feasible and inexpensive means of continuously monitoring residual free chlorine and pH in flowing water. Future research will target further optimization of the microchannel configuration and integration of the photodiode to improve the system's performance.

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