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ARTICLE

Development of a Flow-Batch Analyzer for the On-Site Automated Determination of Residual Chlorine in Drinking Water

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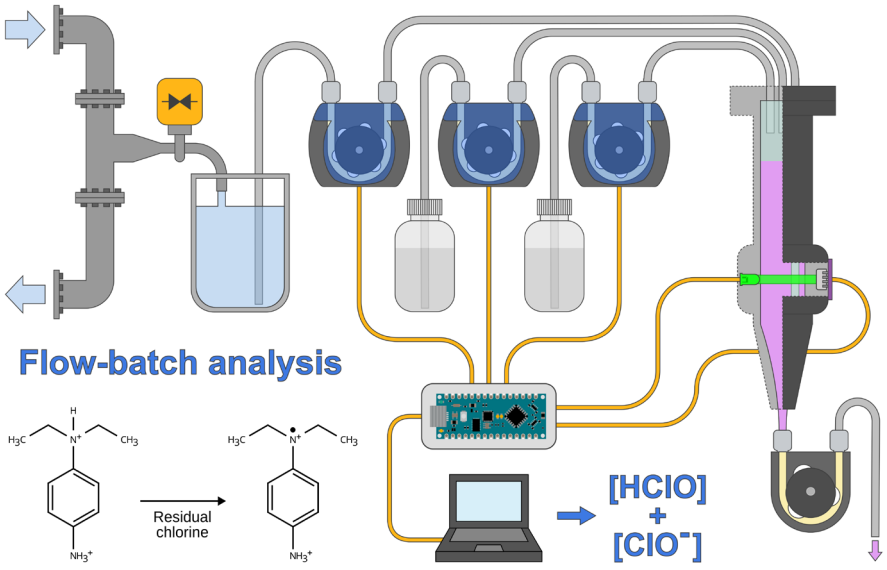

A novel automated analyzer for the determination of residual chlorine in water was developed and evaluated. The analyzer is based on the technique of flow-batch analysis and employs the DPD photometric method for measurement of free chlorine. To decrease complexity, a stirrer was not used for mixing, resorting instead to the turbulence of the fluids to attain a satisfactory mixing of the reactants. The prototype was built using peristaltic pumps, a reaction-detection cell, and an LED-photodiode detection system. The open-source Arduino microcontroller platform was used for data acquisition and control. The operational evaluation of the system included the study of the mixing process, the determination of the optimum concentration of DPD reagent and the calculation of analytical figures of merit: linear range, precision and accuracy of the results, as well as detection and quantification limits. The performance of the analyzer was deemed fit for the purpose of on-site analysis. This prototype is being taken as the basis for the design of an industrial-grade on-site on-line analyzer for the determination of residual chlorine in water treatment plants and drinking water distribution systems.

Keywords: residual chlorine, drinking water, flow-batch, automation, analyzer

INTRODUCTION

The addition of chlorine in water treatment plants and drinking-water distribution systems is a usual practice for the elimination of pathogenic microorganisms. Once dissolved in water, chlorine undergoes

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several chemical reactions. A fraction may react with organic matter and microorganisms as well as with ammonia, generating substances with lower antimicrobial activity, such as monochloramine and dichloramine. The remaining chlorine species are known collectively as “residual chlorine” which is available for further antimicrobial activity. Molecular chlorine remains in a pH-dependent equilibrium with hypochlorite ion and hypochlorous acid:

$$Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^-$$

$$HClO \rightleftharpoons ClO^- + H^+$$

The sum of molecular chlorine, hypochlorous acid and hypochlorite ion is called free chlorine.[1-3]

In drinking-water distribution lines, the decrease in residual chlorine levels along the pipes is detrimental to the desired antimicrobial activity. To maintain the required residual chlorine concentration, water utilities may install rechlorination stations at specific points in the system, ensuring it remains above the minimum threshold.

The concentration of residual chlorine is one of the key quality indicators in drinking water. The World Health Organization (WHO) recommends a minimum concentration of 0.2 mg L^{-1} of free chlorine at the delivery point to ensure an effective disinfection.[4] On the other hand, high levels of free chlorine may produce unacceptable taste and odor, mainly due to byproducts formed through reaction with organic matter. The levels at which undesirable taste and odor become perceptible depend on composition of the raw water, temperature and individual sensitivity, but usually are above 2 mg L^{-1}. Higher levels may even cause health issues. For that reason, maximum levels must also be established. The WHO has set a guideline value of 5 mg L^{-1}, but due to sensorial aspects, local regulatory bodies often establish lower limits. In Uruguay, for instance, Decree 375/2011,[5] based on UNIT Technical Standard 833:2008,[6] establishes a maximum value of 2.5 mg L^{-1} for free chlorine in drinking water.

From an analytical perspective, residual chlorine is determined by measuring free-chlorine levels. Several methods are available, including the amperometric method[7] and the spectrophotometric methods based on N,N’-diethyl-p-phenylenediamine (DPD)[8,9] and syringaldazine.[10,11] The DPD method is dependable and widely established, being listed in the APHA Standard Methods.[12] It relies on the oxidation of DPD solutions by free chlorine, forming a colored substance (Würster dye) with absorption maxima at around 515 and 550 nm. This reaction occurs at pH values around 6. However, in the presence of excess free chlorine, a secondary product, a colorless imine, may be produced. This is undesirable as it affects the quality of the analytical results.

Given the inherent instability of chlorine solutions, residual chlorine should not be determined on stored samples but rather determined on-site. Water treatment plants and drinking-water distribution systems require the use of on-line automated methods to ensure the necessary analytical frequency without the need for manual sampling and analysis.

Different techniques based on flow analysis have been proposed to automate free chlorine determinations. Flow injection analysis (FIA)[13] is the most frequently reported for this purpose.[14-19] This automation technique requires only small sample volumes and can provide high sampling frequencies with good precision, making it suitable for laboratory use and for the development of sophisticated analyzers. However, it is delicate and can be affected by issues such as the presence of gas bubbles as well as from refractive-index (“schlieren”) effects, which are problematic when photometric detection is used. Therefore, it is not the best option for on-site analyzers, where simplicity, robustness and dependability are absolute requirements.

Flow-batch analysis (FBA), first proposed by Honorato[20] and by Gonçalves,[21] is an automation technique that combines characteristics of both flow analysis and traditional batch analysis. It leverages the advantages of both modalities, resorting to in-flow fluid handling while retaining the batchwise styles of mixing and static detection. Although FBA does not achieve the high sampling frequencies of FIA, it has advantages in terms of simplicity and robustness. Reagents and sample are thoroughly mixed in a mixing chamber (usually with the aid of a stirrer), unlike the mixing coil used in FIA. As a result, no concentration gradient is

generated, avoiding the appearance of refractive-index effects. Detection can be carried out in static mode once mixing is complete. In fact, the mixing chamber can also be used as a detection cell, simplifying the design and avoiding the possible interference caused by gas bubbles, which rise to the surface and are easily eliminated.

FBA has been successfully used for several analytical applications in recent years.[22-25] However, a literature search for previous publications on the determination of free chlorine by means of FBA with photometric detection yielded no results. To date, only one paper has been found describing the use of a flow-batch analyzer for chlorine in water but using electrochemical detection.[26]

In this work, we describe the development and evaluation of a novel flow-batch analyzer for the determination of free chlorine in water samples. It was part of a larger project, in partnership with a local technological company, aimed at developing a cost-effective, internet-based network of automated on-line analyzers for the monitoring of residual chlorine, to be deployed in water treatment plants and drinking-water distribution lines. The analyzer was based on the DPD photometric method, utilizing the FBA technique for its inherent advantages, as discussed above. It used low-cost industrial peristaltic pumps, an LED-based detection system, and open-source Arduino-compatible hardware for control electronics. The final product at this first stage was a working prototype capable of performing the on-line determination of free chlorine at specified time intervals and transmitting the results to a PC via a USB port. This prototype can easily serve as a foundation for a more complex system capable of handling internet communications, which is currently being designed.

MATERIALS AND METHODS

Reagents and samples

Anhydrous DPD sulfate (≥ 98.0%) was from Sigma Aldrich (Burlington, MA, USA). All other reagents were also of analytical-reagent grade and obtained from Sigma-Aldrich.

DPD reagent solution was prepared according to APHA method,[12] except for DPD concentration, which was modified as described below.

Chlorine standard solutions were prepared daily from commercial sodium hypochlorite solution (nominal concentration 40 g L^{-1}) which was periodically titrated according to the APHA standard method.[12]

Routine determinations by the manual method were carried out using Macherey-Nagel (Dueren, Germany) Visocolor DPD reagent powder pillows.

Samples of tap water with different levels of residual chlorine were collected from the local distribution system. Some samples were spiked to obtain concentrations in the upper range up to 4 mg L^{-1} free chlorine.

Apparatus

Absorbance measurements in the laboratory were performed using a Shimadzu UV-1900i spectrophotometer fitted with 1-cm quartz cells.

The automated flow system was implemented using three 8-roller Kamoer (Shanghai, China) KCM peristaltic pumps, equipped with 24-V stepping motors and silicone pump tubing (1.61 mm internal diameter).

The reaction-detection cell, 110 mm in length, was constructed from stock 15-mm internal diameter clear glass tubing, fitted with a conical end where the drain pump was installed. The cell was fixed in a vertical position. An opaque shield, 3D-printed with black PLA filament, was used to isolate the cell from ambient light.

The detection system was composed of a high-intensity green LED with a nominal maximum emission at 515 nm (Kingbright, City of Industry, CA, USA) and an OPT101 (Texas Instruments, Dallas, TX, USA) detector/amplifier integrated circuit (IC), both mounted in a lab-made holder, also 3D-printed with black PLA filament. The LED and detector were arranged on opposite sides of the cell.

The final aspect of the cell is shown in Figure 1.

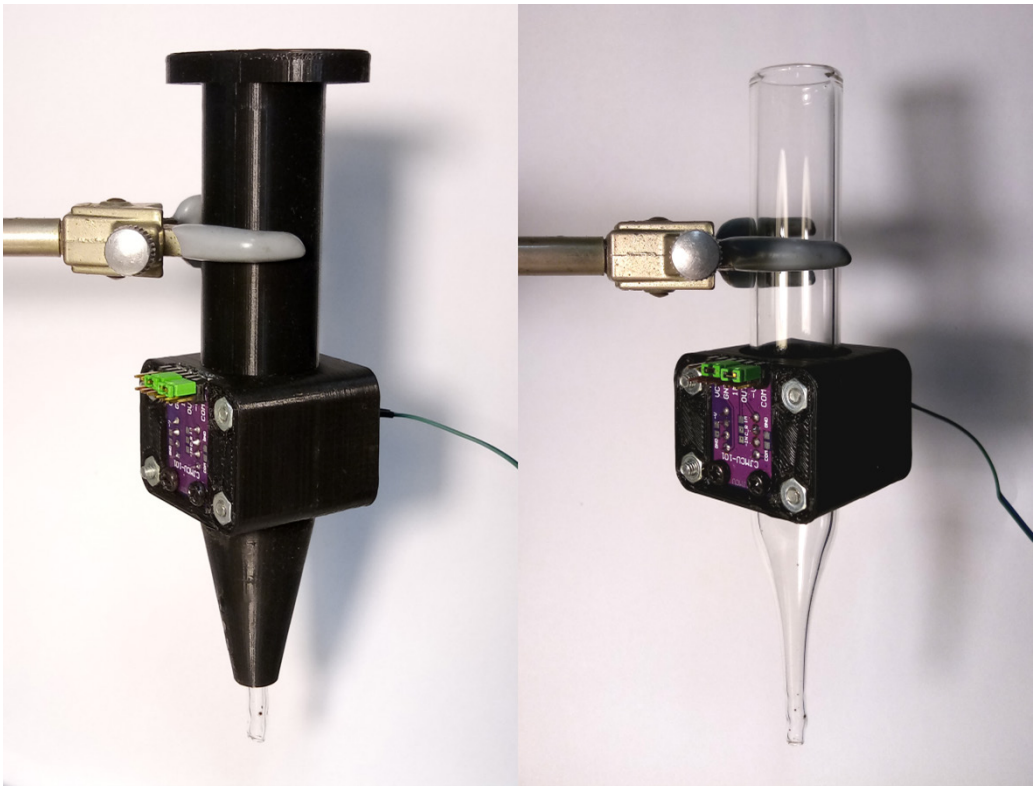

Figure 1. Reaction-detection cell, with and without the light shield installed, shown on the left and right, respectively.

Liquids (DPD reagent solution, buffer and sample) were delivered by the peristaltic pumps (P1 to P3) to the upper end of the reaction-detection cell via three pieces of stainless-steel tubing (0.75 mm internal diameter) fixed in a stopper. The flow rates and times were set at 3 mL min^{-1} for 10 seconds (DPD reagent and buffer) and 30 mL min^{-1} for 20 seconds (sample), corresponding to final volumes of 0.5, 0.5 and 10 mL respectively.

A generic peristaltic pump (P4) was used to empty the reaction cell to waste and also functioned as an effective blocking valve when turned off. Waste was collected in a reservoir for later disposal according to local regulations.

The water samples pumped by P3 were taken from an auxiliary intermediate reservoir which was emptied and refilled when changing samples.

The data acquisition and control system consisted of an Arduino Nano board with an ATmega 328P microcontroller and an ADS1115 (Texas Instruments) 16-bit data acquisition board, which received the analog signal from the OPT101. The ADS1115 was in turn connected to the Nano board by means of the I^2C serial bus.

Control of the stepping motors for the three main peristaltic pumps was achieved with three A4988 digital drivers (Allegro, Manchester, NH, USA), interfaced with the Arduino Nano board. Pulse-width modulation (PWM) was employed to control the drain peristaltic pump via an NPN bipolar junction transistor. A separate transistor switched the LED, powered by an LM334 (Texas Instruments) constant-current source. The operating current of the LED was adjusted to ensure approximately 3.5 V at the output of the OPT101 when the cell was filled with water.

All necessary analytical calculations were carried out by the microcontroller, and the results were then transferred to a notebook computer via the USB connection. Firmware for the microcontroller was written and compiled in the Arduino Integrated Development Environment (IDE). The diagram of the fluidic system is depicted in Figure 2, while Figure 3 represents the schematics of the electronic circuit.

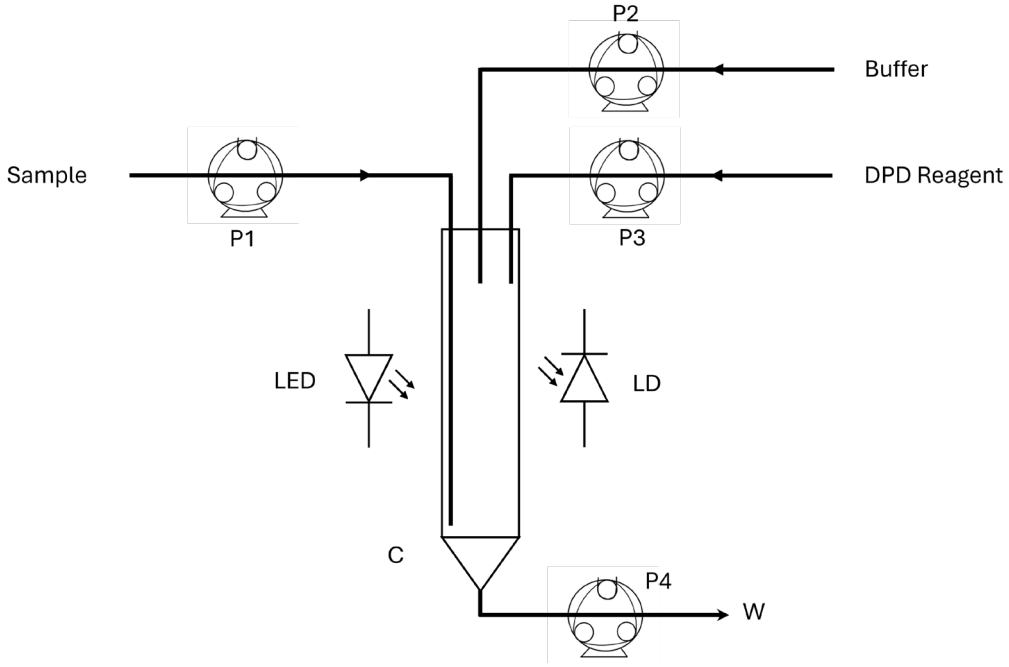

Figure 2. Schematics of the fluidic system. C: reaction-detection cell. P1, P2, P3: main peristaltic pumps. P4: auxiliary peristaltic pump. LED: light-emitting diode. LD: light detector. W: waste.

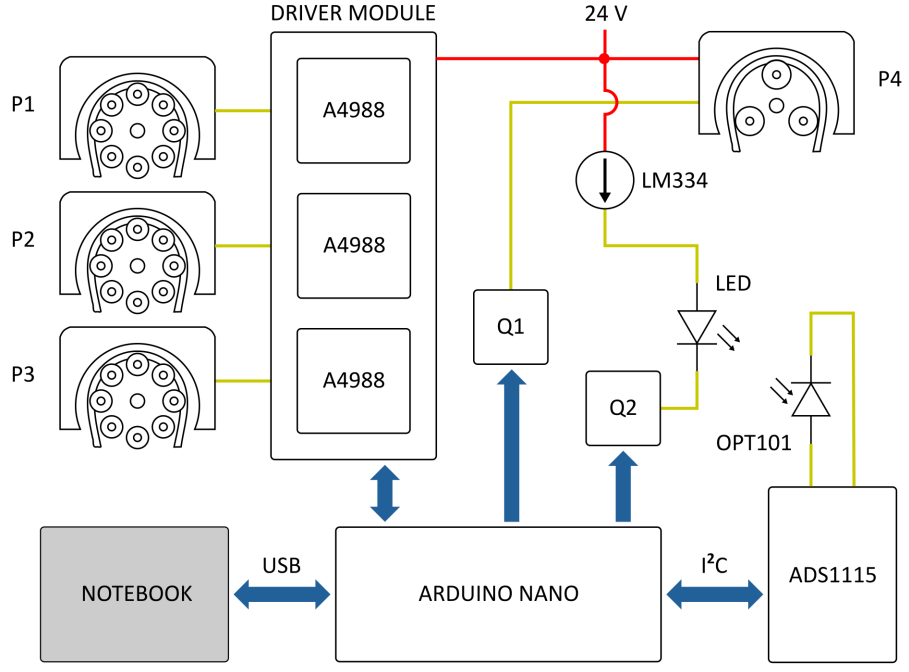

Figure 3. Schematic diagram of the electronic circuit. P1, P2, P3: main peristaltic pumps. P4: auxiliary peristaltic pump. Q1, Q2: NPN transistors.

System operation

The system operates under the control of firmware loaded onto the Arduino microcontroller board. It typically remains in standby mode, with the analytical process initiated at predefined intervals (for example, every three hours), starting with several rinses of the flow system and reaction-detection cell using fresh sample.

The adjustment of the photometric measurement system begins with the LED turned off, measuring and storing the "dark current" signal. Next, with the cell filled up with water, the LED is turned on and the "full scale" (i.e. 100% T) signal is also measured and stored. Once these measurements are complete, the system is ready to begin absorbance measurements.

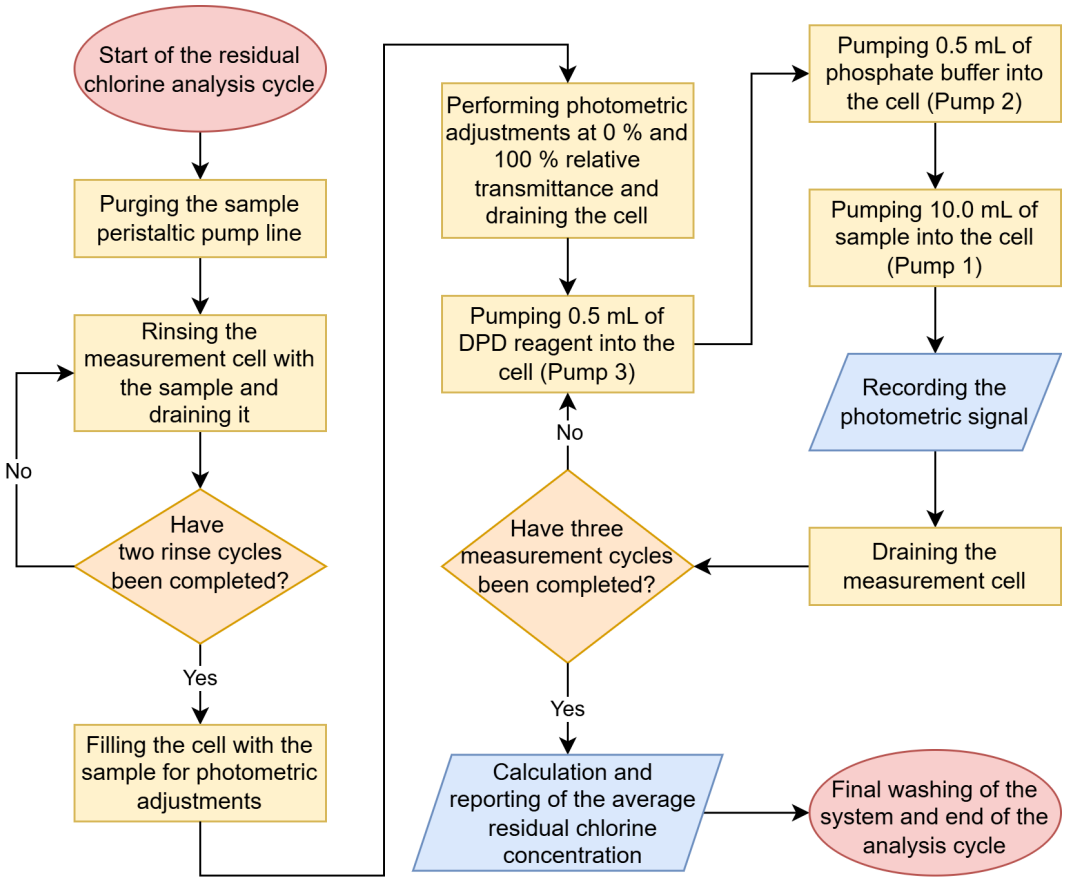

Figure 4. System operation flowchart, according to the selected operating conditions and carrying out the analysis in triplicate.

RESULTS AND DISCUSSION

Given that the final use of the automated system will be under variable temperature conditions, a batch-wise study was conducted to assess the influence of temperature on the reaction. Reagent and buffer solutions and deionized water, as well as the spectrophotometer cell were thermostatted in a circulating water bath. The temperatures studied were 5.1, 20.9, 29.8 and 39.8 °C. For each temperature a 6-point calibration curve was plotted in the 0 – 4 mg L^{-1} range of free chlorine. Chlorine standards, prepared at 10-fold concentrations (held at room temperature), were added to the thermostatted water and reagents in appropriate volumes to achieve final concentrations within the desired range. Measurements were carried out at 515 nm. The slopes of the linear calibration curves at these temperatures ranged from 0.2263 to

0.2384 L mg^{-1}, showing a variability of about 5%. This value was deemed acceptable for on-site use and fit for the intended purpose.

One of the first considerations in the design was ensuring thorough mixing of the reagents and sample. Mechanical stirring is commonly employed in flow-batch systems. However, in this work, for increased simplicity it was decided to avoid the use of a stirrer. Instead, we explored the effectiveness of self-mixing based on turbulence, taking advantage of the high flow rate and volume of the last liquid added, which in this case was the sample itself.

The mixing process was studied by means of videos recorded at short distances, as well as by recording the absorbance signal as a function of time at 100-ms intervals, starting before the sample addition and ending once a stable absorbance was reached (Figure 5). It was found that, for the proposed flow rates and times, after an initial period of chaotic fluctuations due to turbulent mixing, a stable absorbance signal was achieved approximately 30 seconds after the sample was added. Consequently, a 30-second waiting time was incorporated into the software before beginning the measurement of the signals.

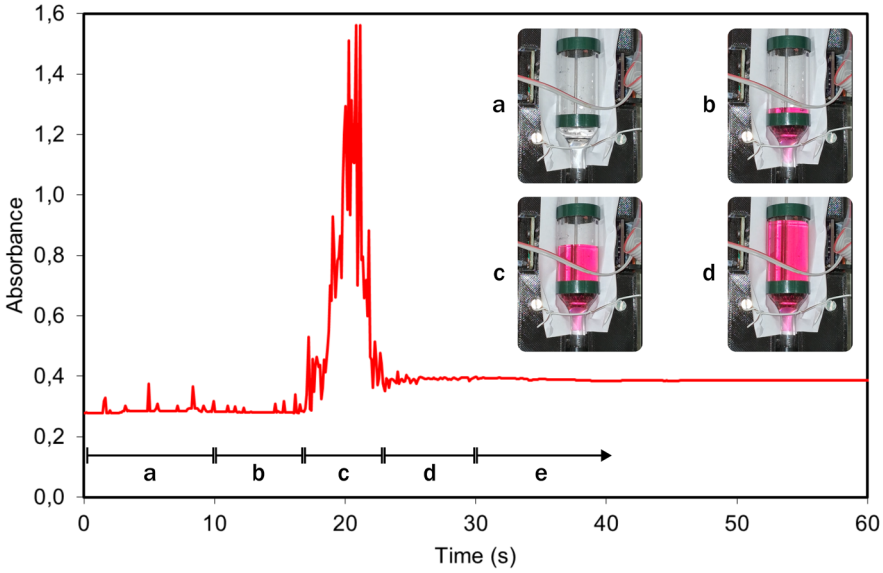

Figure 5. Plot of the absorbance signal (not adjusted to zero) as a function of time during and after the mixing stage, and pictures of the reaction/detection cell (without the detection system and the light shield) taken at different times showing the mixing of reagents and sample. a) Addition of reagent and buffer. b) Beginning of sample addition. Meniscus below the light path. c) Sample addition in progress. Meniscus overlapping the light path. d) End of sample addition. Meniscus above the light path. Mixture remains non-homogeneous. e) Stabilization period prior to absorbance measurement.

During these tests, it was noticed that the vertical position of the nozzle delivering the sample was critical. Due to the high flow rate, a nozzle with its tip positioned too high above the level of the liquid was prone to disperse sample drops, which would adhere to the dry upper portion of the cell wall and affect the analytical performance. To address this issue, the sample nozzle was extended so that its tip remained submerged in the liquid (near the bottom of the cell) from the early stages of the process. This adjustment was found to enhance the mixing effect and prevent sample drops from adhering to the cell wall.

Linearity was checked with standard solutions in the range up to 4 mg L^{-1} of free chlorine. It was found that with the DPD concentration at 1.1 g L^{-1}, the linear range was unsatisfactory, barely reaching 2 mg L^{-1}. Thus, the effect of the concentration of DPD was also studied using concentrations of 4.4, 6.6 and 8.8 g L^{-1} of anhydrous DPD sulfate, corresponding to 4, 6 and 8 times that established in the batch

APHA standard method (Figure 6). The four calibration curves were compared by visual inspection and considering the regression coefficients. A DPD sulfate concentration of 6.6 g L^{-1} was finally chosen as a tradeoff between economy and performance, the calibration equation being A = 0.314 C, R^2 = 0.999. The very slight nonlinearity still observed was ascribed to the use of a cylindrical detection cell and to the polychromaticity of the light emitted by the LED, two obvious potential causes of deviation from Beer's Law.

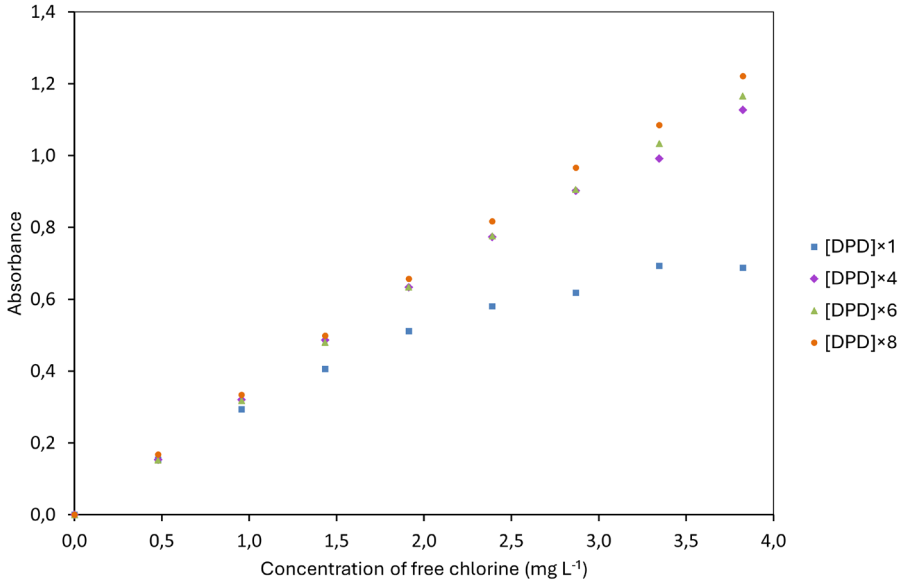

Figure 6. Absorbance as a function of free chlorine concentration at four different DPD concentrations. [DPD]×1 = 1.1 g L^{-1} DPD sulfate.

Once the optimum DPD concentration was determined and linearity evaluated, the remaining analytical figures of merit were studied.

Precision (repeatability) was examined by repeating 10 times the determination of a sample containing around 2 mg L^{-1} free chlorine. The relative standard deviation found was 0.33%.

Carryover between successive determinations was studied in a worst-case scenario by first repeating 5 times the determination of a 4 mg L^{-1} free chlorine solution, followed by repeating 10 times the determination of a blank (deionized water). This experiment was also conducted in the opposite direction, first repeating 5 times the determination of the deionized water blank, followed by repeating 10 times the determination of the 4 mg L^{-1} free chlorine solution. Results are shown in Figure 7.

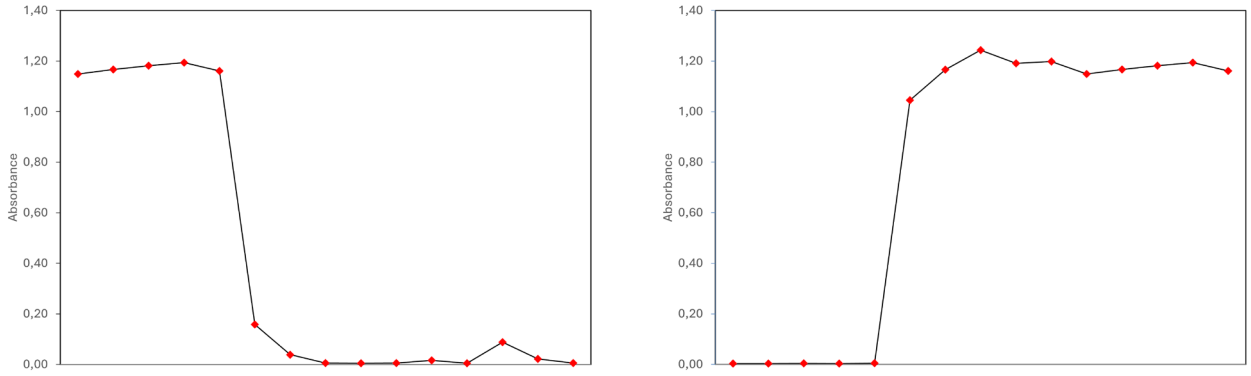

Figure 7. Carryover studies showing the changes in absorbance after a sudden change in free chlorine concentration. The figures show the results of 5 repetitions at the original concentration followed by 10 repetitions at the final concentration. (a) Concentrated sample before blank (b) Blank before the sample.

According to these results, to avoid the memory effect when changing samples, two rinsing steps with the new sample are necessary (loading and discarding each time) before carrying out the determination. Therefore, this routine was incorporated into the software controlling the process.

For accuracy verification, 90 samples with different free-chlorine concentrations within the linear range were analyzed by the proposed automated method and by the manual method using Macherey-Nagel reagent. The correlation curve for the results (automated method versus manual method), presented in Figure 8, fits a straight line ($y = 1.001x + 0.0636$, $R^2 = 0.9936$). It was concluded that the automated analyzer produced results equivalent to those obtained by the manual DPD method.

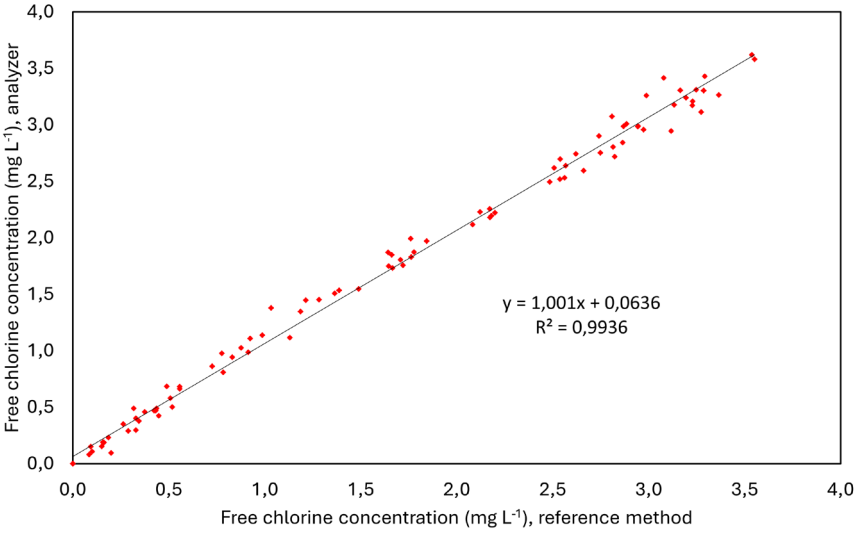

Figure 8. Correlation curve for the results for the analysis of 90 samples by the automated analyzer versus those obtained by the reference batch method with Macherey-Nagel DPD reagent.

Detection and quantification limits were calculated by repeating 10 times the determination of a blank (deionized water) and applying the 3*s* and 10*s* criteria respectively. The limit of detection found was 0.046 mg L^{-1}, while the quantification limit was 0.15 mg L^{-1}.

In each analytical cycle the system consumed 85 mL of water sample, 1.5 mL of DPD reagent and 1.5 mL of buffer. This included the two initial rinsings, photometric adjustment and the analysis carried out in triplicate. The total waste generated per analytical cycle was then 88 mL. Waste was collected in a large reservoir which should be emptied or changed during the periodic maintenance and its content disposed of according to local regulations.

It should be noted that for on-site use calibrations are difficult to automate. This would require not only an additional pump and reservoir (increasing complexity and cost), but also the storage of dilute standard solutions, which are unstable. Thus, it was planned that for field use recalibrations should be carried out simultaneously with periodic maintenance (i.e., replenishment of reagent reservoirs and emptying of the waste reservoir). This approach is usual in commercial automated analyzers for residual chlorine and is an accepted practice in the water industry. Other tradeoffs taken include the use of the water sample itself as the reference for 100% transmittance photometric adjustment, avoiding the need for a deionized water reservoir and an additional pump. This is also common practice in the water industry, but it assumes that the sample is not colored nor contains significant amounts of suspended solids.

The figures of merit obtained during the operation of the automated analyzer were deemed fit for the intended purpose. Unlike laboratory methods, which are carried out under highly controlled conditions, the design and operation of on-site analyzers require several tradeoffs explained above. This, together with the wide ambient temperature range necessarily leads to the adoption of less stringent acceptance criteria for the figures of merit, as compared to usual laboratory methods.

CONCLUSIONS

It was demonstrated that flow-batch analysis is an appropriate analytical technique for automating the determination of residual chlorine in drinking water by means of the DPD photometric method. The system performed correctly without the need for a mechanical stirrer, resulting in increased simplicity.

Therefore, the project is now progressing to the next stage, which involves the design and construction of a robust industrial-grade prototype.

Conflicts of interest

The authors have no conflicts of interest to declare, neither from the funding agency, from project partners nor from other origins.

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