Trial of New Chlorine Analyser

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Abstract

Currently, there are no non-reagent based chlorine analysers approved for use by Water Corporation in pH conditions above 8.5. The HaloMP5 is a new amperometric chlorine analyser claimed to have properties such as pH, temperature, flowrate and pressure independence, self-cleaning abilities, monitoring of 5 parameters, as well as the ability for direct-insertion into main waterlines. A trial of the flow cell HaloMP5 at low flowrates (roughly 25 L/hr) of potable water against the reference analyser (Hach CL17) resulted inconsistent readings with frequent spikes due to the presence of bubbles in the system. A second trial with the direct insertion HaloMP5 under a potable water flowrate of 10 kL/hr (with an air-relief valve upstream) provided more consistent results, averaging 9.31% residual from the Hach CL17 and a 5.31% standard deviation. Longer 2-month trials will need to be conducted to determine the frequency of calibration and cleaning the HaloMP5 requires. More trials are also currently in progress to determine if this accuracy is maintained at higher flowrates, as well as in wastewater conditions, where the pH may be well above 9.

1. Introduction

Amperometric chlorine analysers in use by Water Corporation utilise pH and temperature sensors to adjust for changes in these conditions (Water Corporation, 2022). Testing indicates all approved amperometric analysers struggle to maintain accuracy if the pH conditions are above 8.5. Frequent recalibration and cleaning are also required if fouling occurs (Water Corporation, 2022). The HaloMP5 is a new amperometric chlorine analyser that claims to have several valuable properties (Halogen Systems Inc [HSI], 2022):

- A pH range of 6.5 to 9.
- Self-cleaning abilities.
- Pressure and flowrate independence (up to 14.5 bar and 4 m/s respectively).
- Ability for both wet-tap (i.e. direct insertion into mains) or flow cell insertion.
- Monitors 5 parameters (chlorine, pH, conductivity, oxidation reduction potential (ORP) and temperature).

In addition to trialing the accuracy of the HaloMP5, the overall maintainability, reliability and operational feasibility is of interest before it can be approved for use by Water Corporation. This includes the frequency of recalibration, cleaning, ease of use, and need for specialist training and/or maintenance.

The analysers in this project specifically measure ‘free chlorine,’ which refers to hypochlorous acid (HOCl) and hypochlorite ions (OCl^-) species present in the water (Baker, 1959). HOCl can further disassociate to H^+ and OCl^- depending on the pH and temperature (Baker, 1959; Guigues et al., 2022; Whittle & Lipták, 1994).

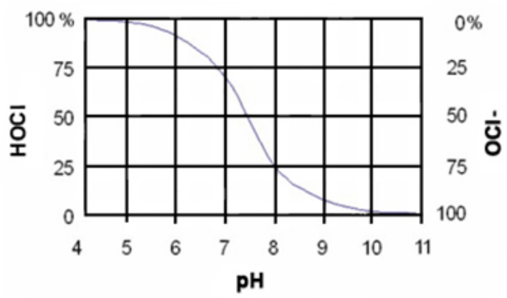

Figure 1 The chlorine dissociation curve (Baker, 1959).

1.2 Amperometric Chlorine Analysers

Amperometric analysers measures chlorine concentration using a platinum cathode (known as the “working electrode”) and a silver chloride anode (or “counter electrode”). A voltage potential is applied on the electrodes so that only a strong oxidizing agent (such as chlorine) produces a current. The following reduction reaction occurs at the working electrode (White et al., 2010):

$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$$

This current is proportional to the chlorine concentration. and must be defined or ‘calibrated’ via a separate, external method. As only the concentration of $HOCl$ is measured at the working electrode, the remaining free chlorine residuals (OCl^-) are estimated by the analyser based on the pH curve in Figure 1. As pH and temperature are directly related to the chlorine species observed in the water, fluctuations negatively affect the accuracy (White et al., 2010). As the concentration is estimated from the volume of water in the flow-cell, the accuracy is also affected by fluctuations in flowrate and pressure (White and Lipták, 1994).

1.3 Colorimetric Chlorine Analysers

Colorimetric analysers uses N,N-diethyl- p-phenylenediamine (DPD) reagent, which react with chlorine to give a pink-ish colour (White et al., 2010). The intensity of the colour is proportional to the chlorine concentration, which is then measured by a spectrophotometer (Patnaik, 2018). The accuracy is affected by the presence of nitrate, iron and manganese substances which readily react with DPD (White et al., 2010), rendering it unsuitable for groundwater applications (Water Corporation, 2022). The Hach CL17sc Colorimetric Analyser is the only currently approved analyser capable of maintaining accuracy in pH conditions above 8.5 (Water Corporation, 2022). It does so using a pH buffer to lower the pH to 6.2 to 6.5, where the reaction ideally occurs. These analysers are inherently flowrate and pressure independent, due to their semi-batch operation, wherein the water is diverted while samples are analysed every 2 to 3 minutes (HACH, 2019).

1.4 Objectives

The objectives of this project are to test the HaloMP5 for its performance and maintainability in three trials:

1. Standard flow cell conditions for potable water to verify the accuracy and reliability.
2. High and variable flowrates of potable water, to test the flowrate and pressure independence.
3. Standard flow cell conditions for treated wastewater, to compare chlorine accuracy and maintenance requirements in wastewater conditions.

In all three trials, the HachCl17 will be act as the reference analyser.

2. Process

2.1 Experimental Facility

The project began with the design of the experimental facility, which can be adjusted to suit all three trials. The setup includes a tank filled with water that is cycled through a loop using a submersible pump.

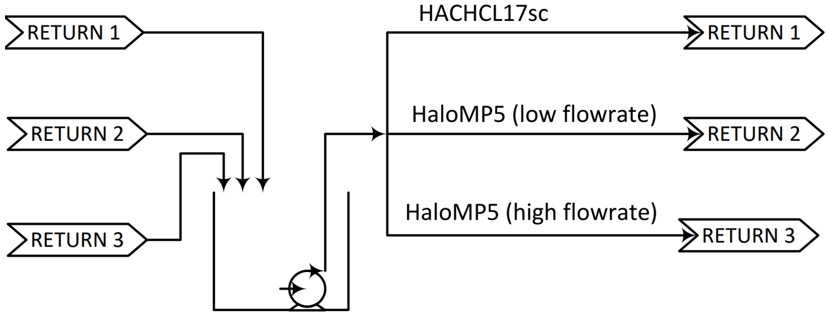

Figure 2 The general layout of the experimental facility.

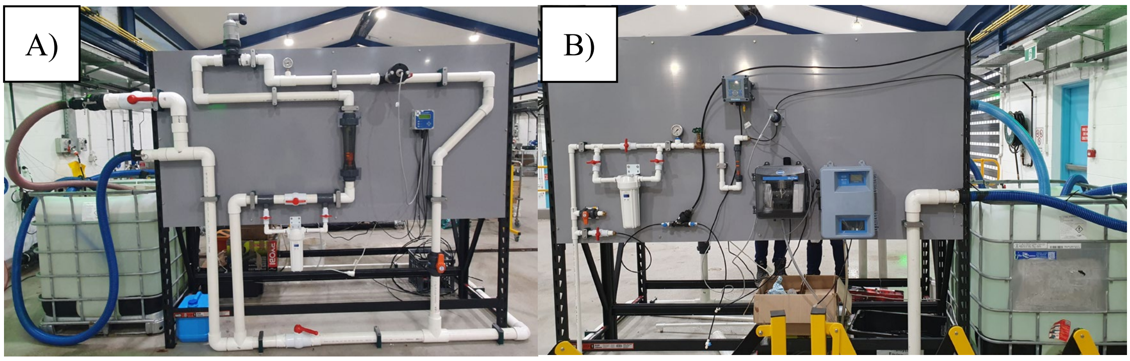

Figure 3 The experimental facility utilised for all three trials. A) The high-flowrate panel, containing the direct-insertion HaloMP5. B) The low-flowrate panel, containing the flow-cell HaloMP5 and HachCl17.

2.2 Trial One: Standard Potable Water Conditions

In trial one, both the HaloMP5 (flow-cell model) and HachCL17 were run under standard analyser conditions (roughly 25 L/hr). Liquid chlorine was dosed once a day using a syringe, at various levels from 0 to 2 mg/L over the course of 8 days. As the water level of the tank would deplete by a quarter everyday due to the waste-stream of the HachCL17, it was replenished once a day.

2.3 Trial Two: High and Variable Flowrates

The direct insertion model of the HaloMP5 was also trialed at chlorine levels from 0 to 2 mg/L over the course of 11 days. The flowrate was maintained at 10 kL/hr through a 50 mm pipe diameter and compared to the HachCL17 at standard analyser flowrates. Portable DPD tests were also conducted daily to verify both analysers are reading correctly. Further testing of the direct-insertion will include higher (up to 35 kl/hr) and variable flowrates (i.e. changing the flowrate every 15 minutes).

3. Results and Discussion

3.1 Flow Cell Model Results

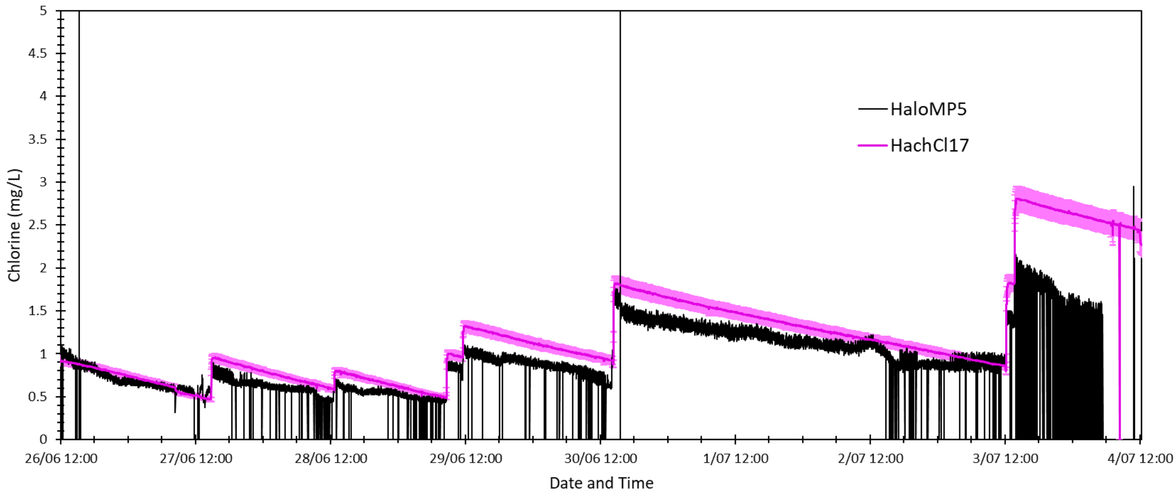

Figure 4 The chlorine measurements from the HaloMP5 flow cell compared with the measurements from the Hach CL17 ±5%.

As the manufacturer specified an accuracy of ±15% (HSI, 2021), and the HachCL17 is rated for ±5% accuracy (HACH, 2019), the target residual (difference between the HaloMP5 and HachCl17) is 20% or lower. The flow cell model started with relatively low residuals, ranging from 0 to 20% during first day. However, the build-up of bubbles in the flow cell caused frequent spikes in the data, and the residuals to increase beyond the 20% target over time. This is due to the presence of air inferring with the electrodes' contact with water, causing it to report zero chlorine. The bubble-buildup also decreases the water volume overtime and consequently the perceived chlorine content drifts away from the expected value. This drifting continued until the 3rd of July, where the HaloMP5 ceased logging data due too much air in the flow cell. Further trials will be needed to determine whether an air relief valve is sufficient to maintain accuracy, or whether a more robust solution such as a bubble de-gasser is required at the inlet.

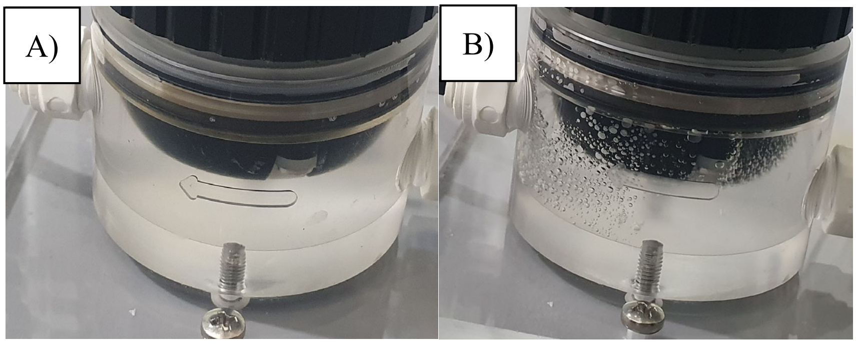

Figure 5 The bubbles in the system gradually build up over time, causing the sensor to decrease in accuracy over time. A) The flow cell at the start of the experiment. B) The flow cell after 24 hours.

3.2 Direct Insertion Model Results

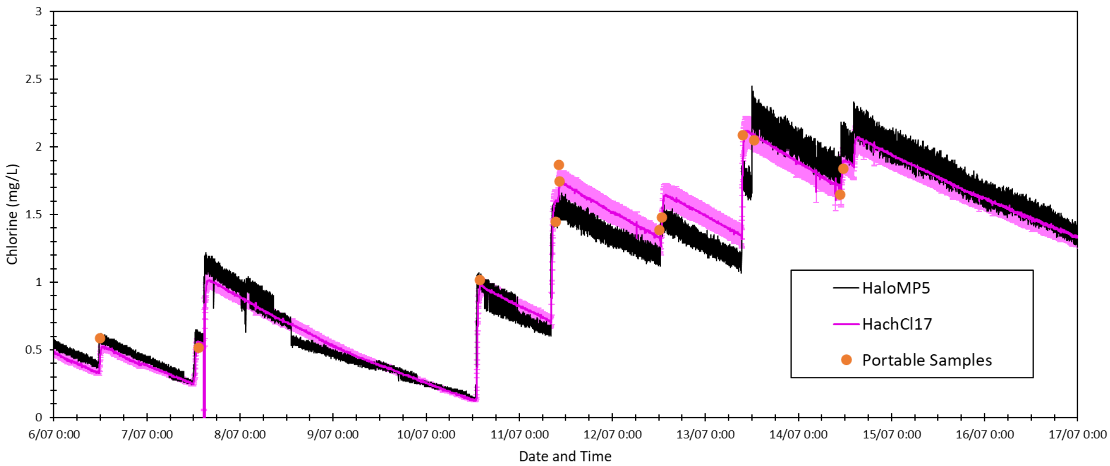

Figure 6 The chlorine measurements from the HaloMP5 direct-insertion compared with the measurements from the Hach CL17 ±5%. The HaloMP5 was recalibrated at 12:00pm, 13th of July.

The direct insertion model was installed with an air-relief upstream to remove trapped air prior to the analyser and reduce false readings due to bubble buildup. Overall the residuals are much more consistent, with no recurring spikes. Recalibration was done after 7 days after noticing the residuals exceeded the 20% target. The accuracy, maximum residual and standard deviation (seen in Table 1) improves with higher chlorine levels, due to the claimed minimum precision of the analyser (0.06 mg/L). The maximum residuals going above the 20% target can also be due to the batch readings of HachCl17 not being representative after dosing, where the chlorine levels may change rapidly.

Chlorine level (mg/L)	Maximum difference (%)	Average difference[1] (%)
<0.5	35.6	9.97 ±6.26
0.5< x< 1.0	26.8	10.0 ±5.43
1.0< x< 1.5	20.7	9.00 ±5.29
1.5< x< 2.0 [2]	19.2	7.03 ±4.78

Table 1 Average, maximum and standard deviation of the relative difference between HaloMP5 and HachCl17 at each chlorine level. 1. Reported error is the standard deviation. 2. The majority of these results are after calibration.

4. Conclusions and Future Work

The HaloMP5 struggles when there are bubbles present as they interfere with the reduction reaction, causing spikes in recorded chlorine and inconsistent accuracy. An air relief valve installed upstream from the direct-insertion HaloMP5 was sufficient to maintain a good accuracy below the target residual of 20%. The HaloMP5 will need to be trialed for a longer period (minimum 2 months as recommended by Water Corporation) to determine other factors such as the frequency of calibration and cleaning needed. The flow cell model would also require another trial to determine if an air-relief valve is sufficient, as lower flowrates are expected to have higher bubble retention. A higher flowrate trial is also in progress, to test the flow and pressure independence, and whether accuracy is maintained to flowrates up to 4 m/s. Additionally, the pH independence will be monitored in wastewater conditions, where the pH can be well above 9.

5. Acknowledgements

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