Development of Tools for Improved Disinfection Control within Distribution Systems
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Research Report No 71
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Research Report 71

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FOREWORD

This is a series of four reports that have been produced in the CRC Water Quality and Treatment Project 2.5.0.1 Development of Tools for the Improved Control of Disinfectant Residual in Distribution Systems.

Report number one is intended to provide persons interested in the design, operation and water quality aspects of water distribution system with an introduction to the project. It describes the aims of the project and provides an overview of the various work packages included in it.

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Report number four is a PhD thesis describing the development and evaluation of a prototype software suite to optimise chemical disinfection control in two full scale distribution systems used as case studies to the project. The software includes an artificial neural network module. The study aims to develop control algorithms that can be used to predict disinfectant residual and chemical dosing requirements. The thesis will be of most value to persons interested in developing knowledge about ANNs. Report 4 was originally published in Modelling of Pollutants in Complex Environmental Systems, Vol 1 (2009) and is reproduced here with permission of ILM Publications.
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Report 1: Introduction and Project Overview

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Research Report Title: Development of Tools for Improved Disinfection Control Within Distribution Systems – Part 1 Introduction and Project Overview

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Project Leader: Christopher Chow and Mike Holmes

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CRC for Water Quality and Treatment Project No. 2.0.2.5.0.1 – Development of Tools for Improved Disinfection Control Within Distribution Systems
EXECUTIVE SUMMARY

The challenging operating conditions experienced by many water utilities in Australia make the supply of good quality drinking water at the customer tap difficult. Supply water may contain elevated dissolved organic carbon (DOC) concentration; water distribution systems (WDSs) can cover large distances; water temperatures can exceed 30°C; and variation in summer–winter flows can be large. Effective and well-operated treatment and distribution barriers are needed. In many cases, the maintenance of a measurable disinfectant residual throughout the WDS is a critical barrier to achieve microbiological compliance. Establishing the optimum disinfectant dose and residual set-point at the outlet of the water treatment plant (WTP) is a complex task. If the dose and residual set-point is too low, disinfectant residual may not penetrate to the end of the WDS and bacterial regrowth can occur. If it is too high, increased disinfection by-product formation, customer complaints, and excessive operating costs may occur. This report provides an overview of a 3½-year collaborative research project undertaken by a number of Australian universities and water utilities aimed at developing tools to improve control of secondary disinfection. The aim of the project is to use data measured using online sensors from locations in the WDS, to predict water quality in advance. The project will identify and develop a range of software and instrumental tools including artificial neural networks (ANN) to optimise disinfection dosing regimes at the WTP and/or booster stations using control theory.
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

1 INTRODUCTION

1.1 Aim

The challenging operating conditions experienced by many water utilities in Australia make the supply of good quality drinking water at the customer tap difficult. Supply water may contain elevated dissolved organic carbon (DOC) concentrations; water distribution systems (WDSs) can cover large distances; water temperatures can exceed 30°C; and variation in summer–winter flows can be large. Effective and well-operated treatment and distribution barriers are needed. In many cases, the maintenance of a measurable disinfectant residual throughout the WDS is a critical barrier to achieve microbiological compliance. Establishing the optimum disinfectant dose and residual set-point at the outlet of the water treatment plant (WTP) is a complex task. If the dose and residual set-point is too low, disinfectant residual may not penetrate to the end of the WDS and bacterial regrowth can occur. If it is too high, increased disinfection by-product formation, customer complaints, and excessive operating costs may occur. This report provides an overview of a 3½-year collaborative research project undertaken by a number of Australian universities and water utilities aimed at developing tools to improve control of secondary disinfection. The aim of the project is to use data measured using online sensors from locations in the WDS, to predict water quality in advance. The project will identify and develop a range of software and instrumental tools including artificial neural networks (ANN) to optimise disinfection dosing regimes at the WTP and/or booster stations using control theory.

1.2 Approaches

The overall strategy taken in the project was to develop individual DrCT® components, integrate them into a functional DrCT®, and evaluate performance in two full-scale WDS case studies. The Myponga WDS in South Australia, operated by United Water International and the Woronora WDS in New South Wales, operated by Sydney Water Corporation, were used as case studies for chlorine and chloramine respectively. The architecture of the DrCT® comprises four main components:

1. A battery of instruments including surrogate disinfectant demand sensors and flow meters will provide water quality and flow data before chemical addition;
2. Disinfection related chemicals will be dosed and mixed using existing operational facilities;
3. Monitors located at strategic locations in the WDS will measure disinfectant residual, flow, and other relevant parameters; and
4. Output signals (from 1, 2, and 3) will be channelled to the ANN, located on a desktop computer, directly accessible to the WTP manager.

The DrCT® concept uses time lagged feed-forward–feed-back signals from online monitors installed at strategic locations in the WDS (Figure 1.1). The large size of most WDSs gives long lag times, often of the order of one to five days or more, and so does not allow simple feed-back control. Signals from sensors located up-stream and down-stream of the disinfectant point of application are relayed to the ANN module. The ANN must be "trained" in order to predict disinfectant residuals at key WDS locations using historic data. Data obtained from continuously measuring online instruments offers the potential to improve prediction performance, and to enable the DrCT® to react to subsequent changes in flow, water quality, or temperature, etc., faster than if daily grab sampling is used. If successful, the DrCT® will assist water quality managers to optimise disinfection set-points, enabling improved performance to be achieved for a wide range of water types even when water travel times cannot be precisely estimated. The project also aims to address a number of key questions including:

1. Does this approach work?
2. What type of sensor or measurement is needed?
3. What is the cost/benefit of using sophisticated online sensors in WDS applications?
2 DEVELOPMENT OF A PROTOTYPE SURROGATE DISINFECTANT DEMAND SENSOR

2.1 Introduction
The aim of this work is to develop a range of sensors that can indicate bulk water chlorine demand (BWCLD) and bulk water chloramine demand (BWCAD) at contact times equivalent to water ages found in real WDSs, online and within a few hours. BWCAD and BWCLD are collectively termed bulk water disinfection demand (BWDD) in this paper. Water quality, including the character and concentration of NOM as well as water temperature, are factors that are known to impact on BWDD. These relationships, together with chlorine and chloramine bulk water decay behaviour, were explored as potential rapid surrogate techniques. The approach taken in this study was to determine the BWDD for a large number of Australian water samples, having a wide range of water qualities, over a 12-month period using conventional laboratory bench techniques. These results were compared with results from rapid surrogate methods. Three rapid surrogate methods were investigated: water quality; temperature elevation; and contact time relationship, and these are described in the following sections.

2.2 Experimental
Water samples from different locations in Australia including New South Wales, Northern Territory, Queensland, South Australia, Victoria, and Western Australia were selected for this study. The water collection programme was organised to collect a batch of 16 samples from selected locations every three months between 2003 and 2004. This selection produced a database of varying water qualities throughout, representing a wide range of Australian water types incorporating raw and treated water as well as seasonal variation. All waters used for this study were sampled prior to disinfection.
General water quality parameters: pH (D-21 & 9620-10D, Horiba, Japan); turbidity (2100AN, Hach, USA); and DOC (820, Sievers Instruments Inc., USA) were determined using the methods described in Standard Methods (APHA, 1998). The UV absorbance at 254 nm (UV254) was measured using a UV/VIS spectrophotometer (UV-1201, Shimadzu, Japan) with a 1 cm quartz cell (APHA, 1998). Colour was determined using the method described in Bennett and Drikas (1993) with a 5 cm cell. Ultrapure water used in these experiments was obtained from a Milli-Q® purification system (Millipore, France).

The rapid fractionation (RF) technique reported in Chow et al. (2004) was used for the determination of four fractions: very hydrophobic acids (VHA), adsorbed by DAX-8; slightly hydrophobic acids (SHA), adsorbed by XAD-4; hydrophilic charged (CHA), adsorbed by IRA-958; and hydrophilic neutral (NEU), that was not adsorbed on any of the ion exchange resins. Chlorine decay was determined by dosing an appropriate volume of a saturated chlorine solution. For chloramination, ammonia followed by chlorine was added at a ratio of 4.5:1 (Cl2:NH3) at pH 8.2 while mixing. Sample size was 2 litres and was stored in an amber bottle at 20°C ± 2°C. At predetermined times 100 mL samples were taken for chlorine analysis over a period of 7 days. Chlorine and chloramine residual was determined using the N,N-diethyl-p-phenylene diamine (DPD) ferrous titrimetric method 4500-Cl (APHA, 1998).

2.3 Result Highlights
BWDD Prediction Using Water Quality Parameter Measurement
An attempt was made to correlate the concentration of RF fractions determined in whole samples with BWDD. Table 1.1 indicates that the VHA fraction, ascribed to humic acids, was the only fraction to show a strong correlation with 3-day BWCLD ($r^2 = 0.88$).

Table 1.1 Correlation of Each Organic Fraction against the 3-Day Chlorine Demand

<table>
<thead>
<tr>
<th>Fraction</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VHA</td>
<td>0.88</td>
</tr>
<tr>
<td>SHA</td>
<td>0.66</td>
</tr>
<tr>
<td>CHA</td>
<td>0.41</td>
</tr>
<tr>
<td>NEU</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 1.2 presents $r^2$ values for correlations between actual BWDD values with DOC, UV254, colour, and VHA for contact times ranging from 1 hour to 7 days. In contrast to the weak correlation found between BWCAD and the water quality parameters investigated, BWCLD demonstrated a strong correlation with a range of parameters ($r^2$ ranged from 0.77 to 0.94). UV254 was identified as the most suitable water quality parameter to act as a surrogate for BWCLD given its strong correlation ($r^2 > 0.93$ for contact times ranging from 1 to 7 days), and the ability to measure UV254 continuously online easily. Results from this study indicate that UV254 can be used as a generic surrogate indicator of BWCLD and it can be applied to a wide range of water sources having an accuracy of +/- 1.0 mg/L. There is potential to improve this substantially if site-specific calibration is made. DOC gave the next best correlation with BWCLD ($r^2 \geq 0.89$) but is more difficult to measure online than UV254. Colour demonstrated a $r^2$ of 0.83 for 1 to 7 days contact time, but with a lower accuracy.
**Table 1.2** $r^2$ Values for Each Water Quality Parameter against BWDD

<table>
<thead>
<tr>
<th>Demand</th>
<th>Water Quality Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Disinfectant</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1-hr</td>
</tr>
<tr>
<td></td>
<td>3-hr</td>
</tr>
<tr>
<td></td>
<td>6-hr</td>
</tr>
<tr>
<td></td>
<td>1-day</td>
</tr>
<tr>
<td></td>
<td>3-day</td>
</tr>
<tr>
<td></td>
<td>7-day</td>
</tr>
<tr>
<td>Chloramine</td>
<td>1-hr</td>
</tr>
<tr>
<td></td>
<td>3-hr</td>
</tr>
<tr>
<td></td>
<td>6-hr</td>
</tr>
<tr>
<td></td>
<td>1-day</td>
</tr>
<tr>
<td></td>
<td>3-day</td>
</tr>
<tr>
<td></td>
<td>7-day</td>
</tr>
</tbody>
</table>

**Figure 1.2** Correlation Between Water Quality Surrogate Parameters, a) DOC, b) UV$_{254}$ and c) Colour and 3-day BWCLD

A multi-linear regression analysis was undertaken using Excel (Microsoft, USA) to investigate if different combinations of surrogate water quality parameters improved the prediction of BWCLD. From the correlation results shown in Table 1.3, no major improvement in BWCLD was found as compared to using UV$_{254}$ alone.
Development of tools for improved disinfection control

Table 1.3 Multiple regression analysis

<table>
<thead>
<tr>
<th>Parameter Combination</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{UV}_{254}, \text{DOC}, \text{Colour}, \text{VHA} )</td>
<td>0.94</td>
</tr>
<tr>
<td>( \text{UV}_{254}, \text{DOC}, \text{Colour} )</td>
<td>0.94</td>
</tr>
<tr>
<td>( \text{Colour}, \text{UV}_{254} )</td>
<td>0.94</td>
</tr>
<tr>
<td>( \text{UV}_{254}, \text{DOC} )</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Contact Time Relationship to Predict BWDD

Disinfectant residual decay curves were established over 7 days in this study with measurements taken at 1, 3, 6, 24, 72, and 168 hours. Regression analysis using plots of short term BWDD (1, 3, and 6 hours contact) against long term BWDD (3 and 7 days) were undertaken, and \( r^2 \) values are summarised in Table 1.4. Figure 1.3(a) presents the relationship between 3-hour and 3-day BWCLD \((r^2 = 0.97)\), and Figure 1.3(b) presents 3-hour BWCAD plotted against 3-day BWCAD \((r^2 = 0.72)\). Excellent correlation was obtained between short contact times BWCLD values (range 1 to 6 hours) and demands measured using long contact times (range 3 to 7 days) as indicated by an \( r^2 \) range from 0.91 to 1.00. Slightly weaker correlations were obtained for BWCAD using this approach with \( r^2 \) values ranging from 0.6 to 0.9.

Table 1.4 \( r^2 \) Values for Short and Long Demand Times

<table>
<thead>
<tr>
<th></th>
<th>Long Demand</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BWCLD 3-day 7-day</td>
<td>BWCAD 3-day 7-day</td>
<td></td>
</tr>
<tr>
<td>Short Demand</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-hr</td>
<td>0.94</td>
<td>0.91</td>
<td>0.69</td>
</tr>
<tr>
<td>3-hr</td>
<td>0.97</td>
<td>0.95</td>
<td>0.72</td>
</tr>
<tr>
<td>6-hr</td>
<td>0.97</td>
<td>0.95</td>
<td>0.77</td>
</tr>
<tr>
<td>1-day</td>
<td>1.00</td>
<td>0.99</td>
<td>0.88</td>
</tr>
<tr>
<td>3-day</td>
<td>-</td>
<td>0.99</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 1.3 Relationship Between 3-Hour and 3-day BWDD (a) BWCLD and (b) BWCAD

An attempt was made to exploit this relationship in order to predict 3-day BWCD by using the contact time coefficients generated in Figure 1.3 (equation will be presented in Part 2 of the report) and the actual 3-hour BWDD (Figure 1.4). Excellent correlation was found for the prediction of BWCLD, particularly for actual chlorine demands of 20 mg/L or less \((r^2 = 0.97)\) with an accuracy of 5 to 10%. Predicted BWCAD showed a weaker correlation \((r^2 = 0.72)\). This confirms that it is possible to predict
WDS-equivalent BWCLD if the WTP BWCLD is known with a high degree of accuracy. A similar approach can be used to predict WDS equivalent BWCAD, but with a lower degree of accuracy.

![Figure 1.4 Predicted BWDD versus Actual BWDD Using Contact Time Relationship Coefficients](image)

**2.4 Temperature Elevation Approach**

An attempt was made to decrease the time required to measure BWDD, by performing bench disinfection experiments at elevated temperature (30, 40, and 50°C) using 3-day contact times. Raw and treated water samples from a South Australian WTP were used for this investigation and results obtained were compared to experiments performed at ambient temperature (20°C). Contact times were determined for elevated temperature experiments that gave equivalent BWDD values to experiments performed at ambient temperature for 3 day contact times. A calibration graph was then established by plotting the natural logarithm (Ln) of contact time versus water temperature, enabling ambient temperature 3-day BWDD to be correlated with water temperature (Figure 1.5). This study showed very promising results for both BWCLD and BWCAD and suggests that by elevating the temperature of a sample and then dosing with disinfectant, the 3-day equivalent BWDD can be determined in a matter of hours, rather than days.
For example, in the case of Myponga raw water - Chlorine (Figure 1.5, upper) it can be seen that the 3-day demand can be reached in just 5.25 hours (Ln 1.65) when the sample is incubated and dosed at 40°C. The same applies to the chloramine prediction for Myponga raw water - Chloramine (Figure 1.5, lower) where the 3-day demand equivalent can be determine in just 5.5 hours (Ln 1.7) when the sample is incubated and dosed at 40°C. Validation of this approach was performed for both chlorine and chloramine using the calibration curves shown in Figure 1.6. This was achieved by comparing BWDD results obtained at ambient temperature with BWDD at 40 and 50°C using predicted contact times. This approach was successfully tested with excellent correlation has been demonstrated between actual 3-day BWDD measured at ambient water temperature and predicted 3-day BWDD measured at 40 or 50°C within a few hours. It is not known at present if this approach is generic for all waters or if a calibration curve must be established for specific water sources, and future work will aim to address these questions.

**Figure 1.5** Temperature – Contact Time Calibration Curves for Myponga Water

**Figure 1.6** Ambient 3 day BWDD versus Predicted BWDD at 40/50°C
2.5 Conclusions in Relation to Disinfectant Demand Development

This study has identified three rapid methods to predict BWCLD and one method to predict BWCAD (Table 1.5). UV$_{254}$ was identified as a potential generic rapid surrogate indicator of BWCLD and a number of commercially available continuous online analysers are available. This study also demonstrated that it is possible to determine the 3-day and 7-day BWCLD rapidly and accurately if the short term BWCLD (e.g. 3 hours) is known together with correlation coefficients. Finally, the elevated temperature method can be used to indicate 3-day and 7-day BWCLD and BWCAD within a few hours.

Table 1.5 Summary of BWDD Surrogate Indicators

<table>
<thead>
<tr>
<th>Water Quality</th>
<th>$r^2$ at 3-day Contact Time</th>
<th>Online</th>
<th>Speed</th>
<th>Continuous or Batch</th>
<th>Generic</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV$_{254}$</td>
<td>0.94 0.36</td>
<td>yes</td>
<td>fast</td>
<td>continuous</td>
<td>yes$^{(1)}$</td>
</tr>
<tr>
<td>Colour</td>
<td>0.83 0.34</td>
<td>yes</td>
<td>fast</td>
<td>continuous</td>
<td>yes$^{(2)}$</td>
</tr>
<tr>
<td>DOC</td>
<td>0.90 0.42</td>
<td>yes</td>
<td>fast</td>
<td>batch</td>
<td></td>
</tr>
<tr>
<td>RF_VHA</td>
<td>0.88 0.45</td>
<td>no</td>
<td>slow</td>
<td>batch</td>
<td>yes</td>
</tr>
<tr>
<td>Contact time</td>
<td>0.97 0.72</td>
<td>no</td>
<td>3 hrs</td>
<td>batch</td>
<td>yes</td>
</tr>
<tr>
<td>Elevated temperature</td>
<td>0.98 0.97</td>
<td>no</td>
<td>3–5 hrs</td>
<td>batch</td>
<td>?</td>
</tr>
</tbody>
</table>

(1) Improved accuracy may be achieved using site specific calibration
(2) Most suited to raw water
3 ASSESSMENT OF COMMERCIALLY AVAILABLE DISINFECTANT RESIDUAL SENSORS

Online disinfectant residual instruments are required for a variety of reasons, including process control of primary and booster chlorination/chloramination, online monitoring linked to supervisory control and data acquisition (SCADA), and offline monitoring usually linked to a data logger. Analysers employed in distribution systems can be permanently installed or relocatable and used for short-term investigations. The aim of this trial was to determine key performance characteristics for a number of commercially available instruments. This section describes the methodology used, and provides some preliminary results obtained for the evaluation of free chlorine analysers.

3.1 Methodology

Nine free chlorine analysers (Table 1.6) were evaluated under laboratory conditions using a methodology based upon the ISO Standard 15839:2003 (ISO 15839:2003). A test rig was constructed at the Australian Water Quality Centre (Adelaide, Australia) in which mains water supplied from Little Para WTP (South Australia) could be recirculated using two submersible pumps (Figure 1.7). Two tanks, A and B, allowed the operator to supply pre-dosed or residual free feed water. Flow rate was controlled using a flow meter and diaphragm valve. The analysers were connected to the system via a manifold and series of valves. Where the analyser did not spoil the sample, test water was returned to the supply tank. Chemicals were dosed and mixed to water in the supply tank to achieve the required concentrations of chlorine, ammonia, and alkalinity. Chemical interference tests were also undertaken for pH, DOC, conductivity, iron, and manganese. The output from online instruments, as well as sample temperature and pH, was logged using a 16 channel datalogger (Prologger 7001, MEA, Australia). During the trial, all analysers were calibrated using a 1 mg/L free chlorine calibration solution. Disinfectant residuals were analysed using methods described in ISO 8466-1 (1990).

### Table 1.6 Free Chlorine Analysers

<table>
<thead>
<tr>
<th>Analyser</th>
<th>Measurement Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hach CL17</td>
<td>Colorimetric</td>
</tr>
<tr>
<td>Yokogawa Model FC400G</td>
<td>Polarographic</td>
</tr>
<tr>
<td>Prominent Dulcometer D1C</td>
<td>Amperometric</td>
</tr>
<tr>
<td>Applikon ADI 2019</td>
<td>Colorimetric</td>
</tr>
<tr>
<td>B&amp;C Model CI7685</td>
<td>Potentiostatic Sensor</td>
</tr>
<tr>
<td>Endress &amp; Hauser CCS141</td>
<td>Amperometric</td>
</tr>
<tr>
<td>Wallace &amp; Tieman Depolox 3+</td>
<td>Amperometric</td>
</tr>
<tr>
<td>Wallace &amp; Tieman Depolox 4 &amp; MFA</td>
<td>Potentiostatic Electrode</td>
</tr>
<tr>
<td>ATI A15</td>
<td>Polarographic</td>
</tr>
</tbody>
</table>
3.2 Results and Discussion

As an example, results are presented for free chlorine residual analysers. For the purposes of this paper, results from individual analysers evaluated in this study are not named. For consistency, analysers have been given a code (1–9). Figure 1.8 presents a typical graph of a free chlorine monitor’s response during trials for the determination of response and delay times. In this test, analysers were subject to a series of alternating low (20% span, corresponding to 0.4 mg/L) and high (80% span, equivalent to 1.6 mg/L) free chlorine residuals.
Response time is a very important parameter when a monitor is used in a control loop. Mean response times for a positive change ranged from 42 to 202 seconds (Figure 1.9). Instruments having quick response times are required for control applications. If, however, monitoring only is required, analysers with more sluggish response can be used.

Figure 1.9 Analyser Response Times to Positive and Negative Change in Sample Concentration

Instruments demonstrated variable responses during interference experiments. Figure 1.10 shows the response of the 9 analysers evaluated using a sample concentration of 1.0 mg/L free chlorine with conductivity ranging from 286 to 819 µS.

Figure 1.10 Response of Free Chlorine Analysers during Conductivity Interference Tests

The impact of sample pH ranging from pH 6.0 to 9.0 on analyser performance when presented with a 1.0 mg/L free chlorine sample was found to be variable (Figure 1.11).
Figure 1.11 Response of Free Chlorine Analysers during pH Interference Tests

Manganese and iron also impacted the performance of some analysers (Figures 1.12 and 1.13). This effect may become more pronounced during long term deployment when subjected to water with elevated concentrations of iron or manganese.
Development of tools for improved disinfection control

Figure 1.12 Response of Free Chlorine Analysers during Manganese Interference Tests

Figure 1.13 Response of Free Chlorine Analysers during Iron Interference Tests

Mean values and standard deviation for a day to day repeatability test using a 0.7 mg/L free chlorine sample over an 18 day period are presented in Figure 1.14.
The free chlorine analysers evaluated in this study demonstrated a range of $r^2$ values for linearity over the range 0 to 2 mg/L. All monitors showed non-linear relationships to varying degrees (Figure 1.15).

Limit of detection (LOD) ranged from 0.03 to 0.1 mg/L and limit of quantification (LOQ) ranged from 0.1 to 0.32 mg/L. The importance of this can be demonstrated using the following example. If analyser 7, which showed a LOQ of 0.22 mg/L, indicates a result of 0.5 mg/L, the result is actually within the range 0.39 to 0.61 mg/L.
Figure 1.16 Free Chlorine Analyser Limits of Detection and Limits of Quantification

3.3 Conclusions in Relation to Assessment of Commercially Available Sensors

The free chlorine analysers evaluated in this trial used a range of measuring techniques, some of which are directly related to Standard Methods (APHA, 1998) while others use modified or even alternative techniques. This, together with sample water chemistry, may lead to differences in results between laboratory methods and online analysers. All analysers evaluated demonstrated drift, non-linearity, and interference effects. Instruments may be required for a range of duties, such as control of chlorination or for long term monitoring in remote locations. Instrument performance characteristics are a key consideration when selecting an instrument for a particular application. This study concluded that it is beneficial to determine the key performance indicators for a disinfectant residual analyser to ensure it is suitable for a particular application.
4 ANN MODEL DEVELOPMENT

A common approach that has been adopted for water quality modelling is the coupling of a mass balance (with chemical reaction) to a hydraulic model of a WDS. Simulation models have been used extensively for simulation, analysis, and control applications. WDSs are complex hydraulic systems consisting of tanks, pumps, and valves connected by a network of pipes. The mathematical models that govern the flow of fluids within individual pipes, tanks, and pumps are then solved iteratively in order to derive a model that describes the WDS over a period of time. This approach to modelling water quality has led to the development of popular water quality modelling packages such as EPANET (Rossman and Boulos, 1996) and WaterCAD (Walski et al., 2003).

Despite the applicability of simulation models to WDS design and analysis, these models have disadvantages when applied to disinfection residual control. First, to gather the required information and then construct, calibrate and validate a hydraulic model of even a small WDS requires a significant investment in terms of time and effort (and therefore money). For smaller water utilities, this modelling approach may be cost prohibitive. Second, simulation models rely upon the selection and calibration of an appropriate model for disinfection residual decay within pipes. The first-order decay model is often selected as the default choice (Walski et al., 2003). Recent studies have found that models that are more complex may better represent the various chemical processes that contribute to the decay of disinfection residual (Salhane, 2002). However, there do not appear to be any firm guidelines (other than a trial-and-error approach) upon which to base the selection of an appropriate decay model, as results have shown that different models are capable of describing decay under different conditions. Finally, a third disadvantage of simulation modelling is the computational effort required to run a single simulation, let alone successive simulations. In assessing the performance of control systems using simulation models, Lobbrecht and Solomatine (2002) have suggested that, for large networks, the computational time required to determine an optimal value of the controlled variable will exceed the time allowed, and that computationally faster methods should be sought for this application.

4.1 Empirical Modelling

In the case of either a complex, non-linear system, or where there is some uncertainty regarding the system, it is often more expedient to develop an empirical model that describes the observed behaviour. However, this expediency is gained at the expense of any insight that might be derived from the development of a physical model. Empirical models are generally “black-box” models, wherein the internal parameters are not necessarily directly related to the underlying process being modelled, but rather simply take values that allow for the most accurate fit to the observed behaviour of the system in question. For the purposes of modelling water quality within a control framework, the use of empirical models is a more than acceptable approach, since the objective is to simply obtain a statistical model that can accurately describe the input-output (I/O) behaviour of a given WDS (Uber et al., 2003).

The identification of suitable I/O models based on observed system behaviour is a well-established field and has been used extensively to develop control systems for complex chemical processes. Conventional system identification assumes a linear model, ranging from a simple least-squares linear regression (LR) to a more complex model such as the auto-regressive moving-average (ARMA) models. The application of this conventional approach was demonstrated for a simulated WDS with promising results (Uber et al., 2003). However, since the dynamics of a WDS are non-linear, conventional linear models fail to accurately describe the observed non-linear behaviour, in particular when the system includes common inlet-outlet storage tanks.

Identification of non-linear models using conventional techniques is inherently difficult. Recently, however, the development of more empirical models using artificial neural networks (ANNs) has been found to be a suitable alternative for the identification of non-linear processes including WTPs and WDSs. The benefits of using ANNs are primarily that they can describe non-linear behaviour more accurately than conventional linear models, and yet are just as easily developed.

The development of ANN models within a water quality context has been examined previously for modelling of disinfection residual (Bowden et al., 2003; Rodriguez and Sérodes, 1999; Sérodes et al., 2001), THM evolution, and WTP performance. However, these studies are relatively few in number in
comparison to the extensive use of ANNs within a broader context. The refinements to the ANN development methodology remains an ongoing focus of research that aims to develop a robust ANN development framework.

The application of a current ANN development framework was examined for the Myponga WDS, South Australia. The following sections describe the development of a general regression neural network (GRNN) to provide a +24-hour prediction of downstream chlorine residual based on observations of the Myponga WDS made over a six-month period.

4.2 Case Study

The Myponga WDS is situated approximately 60 km south of Adelaide, South Australia, and serves a connected population of approximately 60,000 customers. Raw water is sourced from the nearby Myponga Reservoir and is treated using flocculation and coagulation followed by dissolved air flotation/filtration (DAFF). The treatment plant has a design capacity of up to 50 ML/d. Primary disinfection via chlorine injection occurs immediately upstream of two hydraulically balanced 10 ML filtered water storage tanks (FWSTs) and treated water is supplied to the network via the Myponga trunk main.

The network topology, as shown in Figure 1.17, is a branched system with reticulation networks supplied via a central trunk main. The scope of this study was an approximately 20 km span of the Myponga trunk main, from the point of primary chlorine injection at the Myponga WTP (PLM6), trunk main at Cactus Canyon (PLM2) to the Willunga branch main offtake point at Aldinga Road, marked as PLM3. (PLM means pipeline monitoring).

Figure 1.17 Myponga WDS, South Australia

4.3 Data Collection

Current methodologies for the development of ANN models require that sufficient data are collected to describe all seasonal trends in the behaviour of a WDS. A 12-month period would therefore be the minimum required for this purpose. The data for this case study were collected over only a six-month
period, however this period extended from the beginning of February 2003 to the end of July 2003, and therefore captured the variation between summer and winter operating conditions, respectively.

Sources of online hydraulic and water quality data were the SCADA system at the WTP, the South Australian metropolitan water supply telemetry network, and field monitoring stations that were installed for the specific purpose of collecting data for this study. Hydraulic data comprised trunk-main outlet flow from the FWSTs, FWST level, and flow at a major pumping station offtake downstream of the FWSTs.

The online water quality monitored at the WTP consisted of the chlorine residual immediately downstream of the primary chlorine injection point, filtered water turbidity, and pH before and after caustic adjustment. Data were retrieved from the SCADA system at a frequency of 15 minutes.

Three additional PLM sites were also established to provide a profile of water quality along the 20 km section of trunk main that was considered within the scope of this study. The monitoring locations comprised chlorine analysers that enabled logging of free chlorine residual and temperature at 5 minute intervals. Figure 1.17 shows the positioning of the PLM sites along the Myponga trunk main.

4.4 ANN Development

The total available data were processed to validate and, where possible, correct any erroneous measurements. In the case of a few extended (greater than 10 minutes) gaps in the data at several locations, these data were omitted from the data set. Finally, since the time-step was intended to be 1 hour, the various 5, 10, and 15 minute values were smoothed into hourly moving averages.

In total, a data set was generated comprising 2,821 hourly observations of nine parameters (Table 1.7). Lagged parameters (observations at time \( t-1, \ldots, t-d \)) were generated for a maximum delay, \( d \), of 48. Since the time-step within the data was one hour, this generated a new data set comprised of 2,773 observations that represented historical patterns spanning 48 hours.

<table>
<thead>
<tr>
<th>Input</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>WTP.Cl, t-1, ... , t-48</td>
<td>WTP filtered water free chlorine residual, mg/L</td>
</tr>
<tr>
<td>WTP.pH, t-1, ... , t-48</td>
<td>WTP filtered water corrected pH</td>
</tr>
<tr>
<td>WTP.NTU, t-1, ... , t-48</td>
<td>Filtered water turbidity, NTU</td>
</tr>
<tr>
<td>FWS.Lvl, t-1, ... , t-48</td>
<td>Filtered water storage level, %</td>
</tr>
<tr>
<td>PLM6.Cl, t-1, ... , t-48</td>
<td>Free chlorine residual at PLM6, mg/L</td>
</tr>
<tr>
<td>PLM6.Temp, t-1, ... , t-48</td>
<td>Water temperature at PLM6, °C</td>
</tr>
<tr>
<td>PLM3.Cl, t-1, ... , t-48</td>
<td>Free chlorine residual at PLM3, mg/L</td>
</tr>
<tr>
<td>Q.PLM6, t-1, ... , t-48</td>
<td>FWS trunk main outlet flow, ML/d</td>
</tr>
<tr>
<td>Q.PS, t-1, ... , t-48</td>
<td>Sellicks Hill PS flow, L/s</td>
</tr>
</tbody>
</table>

Calibration and validation requirements for ANN models deem it necessary to split the total available data into three subsets for training, cross-validation, and validation. The first two data sets are utilised during model calibration. Training data provide the “experience” that enables the ANN to “learn” the mapping between model inputs and output, which is essentially a calibration of the internal ANN parameters. Over-fitting occurs when the ANN learning goes beyond representing the general I/O relationship in the data, and begins to model the idiosyncrasies that are specific to the data provided. Cross-validation data are also used to independently crosscheck the model accuracy during training to ensure that the model is not over-fitted. The validation data provide an independent data set that
can be used to assess the final performance of the model, since those data are not used within the model calibration.

It is important that each data subset remains representative of the behaviour of the WDS. Hence, the subsets must be divided in a way such that they are statistically similar to each other and also preserve the characteristics of the total data. In this study, a genetic algorithm (GA) (Bowden, 2003) was used to divide the 2,773 historical patterns into training, cross-validation, and validation subsets that comprised of 64%, 16%, and 20% of the total data, respectively. Near optimal division of the data into these subsets was achieved by minimisation of the difference between the distributions of each parameter across the three subsets, which was measured by the Kolmogorov–Smirnov statistic.

The lagging step expanded a set of nine available model inputs into a set of 432 potential candidate inputs. Many of the inputs were correlated and therefore redundant, while other parameters had no correlation with the +24-hour chlorine residual. Hence, the next stage of model development was to apply a selection algorithm to produce a minimal set of inputs that would fully describe the I/O relationship and eliminate any redundant or insignificant inputs. In this study the stepwise partial mutual information (SPMI) algorithm was applied to the 432 inputs against the +24 hour free chlorine residual data (Sharma, 2000).

Calibration of a GRNN model required the optimisation of a single parameter that represents the weighting of historical patterns that is used to determine the output prediction from the network. The optimisation used a single-dimensional hill-climbing optimisation based on minimisation of the mean square error (MSE) of the cross-validation predictions.

The performance of the GRNN developed for the Myponga system was assessed based on prediction accuracy for a set of independent validation data. Several measures of accuracy are typically adopted for the evaluation of statistical or empirical models, however for this study the measures used were the root-mean square error (RMSE), the mean absolute error (MAE), and the Pearson correlation ($r^2$). Each of these measures provided an estimate of the average deviation of the GRNN predictions from the actual observed value. As the time order of observations is not preserved during the data division stage of ANN development, it was not possible to generate a time-series plot of purely validation predictions, and the methodology applied presents the performance graphically as a scatter plot of corresponding predicted versus actual free chlorine residuals (see Figure 1.18 below).

### 4.5 ANN Performance

In total, three models were developed using the available data. Firstly, a GRNN (G1) was developed using only parameters that were measured downstream of the FWSTs. Hydraulically, the scope of the WDS in this instance was simplified, in particular for winter periods, by removing the dynamics of the FWSTs.

A second GRNN (G2) was also developed that included the FWSTs within the modelling scope. It was considered that since the applied chlorine dose would be of interest for control purposes, then this would be a more appropriate model for future controller development. However, the model would need to be able to account for the dynamics of flow within the FWSTs. Low demand, discontinuous WTP operation, and short-circuiting of flows can lead to non-linear behaviour of chlorine residuals downstream of the FWSTs. The purpose of this study was to observe the level of accuracy gained for a more complex WDS. In addition, PLM2 data were excluded to examine the effect of reduced online monitoring of chlorine residual, since most WDSs have fewer monitoring locations than the case study WDS at Myponga.

Finally, a least squares multiple linear regression (MLR) model (M1) was developed using the model inputs selected for the second GRNN model (since the input selection was independent of the choice of statistical model). This provided a comparison of the non-linear ANN approach to the more conventional LR approach.

Graphical results for all three models are shown in Figure 1.18. Figure 1.18(a) shows the performance of the model G1, indicating actual versus predicted free chlorine residual at the PLM3 site, 24 hours in advance. Figure 1.18(b) shows the same plot for model G2, and Figure 1.18(c) for model M1. Model
performances are summarised in Table 1.8, which shows the various measures of performance obtained for predictions based on the validation input data. All three models are highly accurate, however the comparison between Model G2 and Model M1 indicated the superior performance of the (non-linear) GRNN over its linear counterpart. This was found to support several previous studies that also found ANNs to yield much higher accuracy than conventional linear statistical water quality models (Bowden et al., 2003; Sérodes et al., 2001).

The differences in performance between models G1 and G2 indicate that the availability of a more detailed chlorine residual profile was partly responsible for the superior performance of model G1. However, the reduction in performance observed for model G2 was only marginal and, in terms of absolute accuracy, the G2 model still produced very accurate predictions. Considering that most online analysers can only measure to 0.1 mg/L accuracy, an MAE < 0.1 was an acceptable level of performance.

The absolute accuracy of the ANNs was comparable to that obtained in previous studies, which reported models with \( r^2 \) values of 0.95–0.96 (Sérodes et al., 2001). However, the scope of the system modelled in this study combined both the trunk main and FWST components, whereas the previous studies considered these components separately.

<table>
<thead>
<tr>
<th>Data</th>
<th>GRNN Model G1</th>
<th>GRNN Model G2</th>
<th>MLR Model M1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( r^2 )</td>
<td>RMSE</td>
<td>MAE</td>
</tr>
<tr>
<td>Training</td>
<td>0.9902</td>
<td>0.033</td>
<td>0.023</td>
</tr>
<tr>
<td>Testing</td>
<td>0.9722</td>
<td>0.054</td>
<td>0.020</td>
</tr>
<tr>
<td>Validation</td>
<td>0.9752</td>
<td>0.056</td>
<td>0.026</td>
</tr>
</tbody>
</table>

4.6 Future Research
The case study presented in this paper, along with the previous studies cited within, convincingly demonstrate the successful development of accurate models of water quality using techniques based
upon ANNs. The success of this application comes through the reliable collection of data that can be made available for development of such models, and the application of a robust development framework that maximises the accuracy of the models produced. The immediate pathway for future research aims to further develop the data analysis and data processing methods that are employed within the model development framework, such as input selection and data division algorithms.

Reliable and accurate monitoring of parameters throughout a WDS is an important focus if future models are to be developed with high quality data sets. Currently, the ability of a model to be developed is restricted by the ability to measure, online, the required water quality parameters. For applications such as chloramination, where free ammonia concentration is important, advances in measurement technology are required to make suitable data available for the ANN application described in this paper.

The development of intelligent control systems based on ANN process models is another avenue of research that has yet to be extensively investigated from the viewpoint of WDSs and water quality control. ANNs offer a number of advantages when used as a process model within a control model framework. These are, namely, the ability of ANNs to efficiently describe non-linear system behaviour and the ability to continually adapt as new observations are generated. Two models for intelligent control, that make different use of the learning capabilities of ANNs, are inverse process control and model-predictive control (Psichogios and Ungar, 1991).

Inverse process control exploits the ability of ANNs to map the inverse process model (i.e. the relationship between downstream targets and required set-point dose). The model output from an inverse ANN is therefore the control action that is required to achieve the target downstream disinfection residual, which is an input to the model. Although the model for control is reasonably straightforward, this approach requires the development of both a forward and an inverse ANN.

Model predictive control is based on the optimisation of disinfection residuals that are predicted over a specified control horizon (say, the next 12 or 24 hours). In this case, a prediction is generated for each look-ahead step by the model based upon a given control input (chlorine dose). An optimisation algorithm then seeks to minimise the deviation between predicted disinfection residuals and the required target over the entire control horizon. A number of optimisation schemes could potentially be employed depending on the number of inputs and outputs.

Given the high accuracy of predictions that can be obtained using ANN water quality models, future research will be undertaken to examine the performance of intelligent controllers that are based around ANN models.
5 CONCLUSIONS

The concept for the application and development of DrCT® in a full scale water distribution systems has been presented. The system is modular and can be developed and applied in stages, for example, online disinfectant residual analysers can be deployed in the distribution system and BWDD can be assesses using several techniques. Initial results indicate that the DrCT® concept is a feasible one. Key findings from the study so far indicate that:

- $\text{UV}_{254}$, contact time, and elevated temperature demand relationships, are three potential rapid surrogate methods to determine bulk water chlorine demand;
- The elevated temperature technique can also provide a rapid surrogate indication of bulk water chloramine demand;
- The selection of online monitors for long term use in water distribution systems applications is important, given that there was a wide difference in performance characteristics demonstrated in this study under laboratory conditions, e.g. varying limits of quantification (maximum of 0.3 mg/L);
- The use of online monitors is necessary for artificial neural network development; and
- The general regression neural network described above is able to accurately predict in advance chlorine residuals downstream in a real water distribution system.

In the next two years, the Cooperative Research Centre for Water Quality and Treatment research project 2.5.0.1 Development of Tools for Improved Disinfection Control within Water Distribution Systems aims to make advances on all aspects of the research and application as described above. These include:

- Evaluating the rapid surrogate disinfection demand techniques in water distribution systems in the field;
- Evaluating instruments suitable for use in chloramine distribution systems;
- Extending the artificial neural network methodology to the prediction of chloramine residuals in a real water distribution network; and
- Developing control theoretical algorithms for the determination of dosing set-points using chlorine and chloramine residuals predicted in the water distribution system by the artificial neural network.

6 ACKNOWLEDGMENTS

The authors wish to thank: Kathryn Clarkson (Power and Water Authority, NT); Ken Tuner (Gippsland Water, Victoria); Vince Sweet (SA Water Corporation, South Australia); David Smith (Gold Coast Water, Queensland); Shane Hayden, Noel Miles, Robert Considine, and Simon Wilson (Melbourne Water Corporation, Victoria); Dammika Vitanage, Corinna Doolan, and Phil Duker (Sydney Water Corporation, New South Wales); Neil Crossing (United Water International, South Australia); and Kevin Xanthis and Richard Walker (Water Corporation, Western Australia) for their support with this project.
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

7 REFERENCES


Kirmeyer G; Martel K; Thompson G; Radder L; Klement W; LeChevallier M; Baribeau H; Baribeau A (2004). Optimizing Chloramine Treatment. Denver CO: AwwaRF and AWWA.


Report 2: Development of a Surrogate Disinfectant Demand Sensor

Fiona Fitzgerald and Christopher Chow

Australian Water Quality Centre, Adelaide
FOREWORD

This is report number two of a series of reports that have been produced in the CRC Water Quality and Treatment Project 2.5.0.1 Development of Tools for the Improved Control of Disinfectant Residual in Distribution Systems.

Report number one is intended to provide persons interested in the design, operation and water quality aspects of water distribution system with an introduction to the project. It describes the aims of the project and provides an overview of the various work packages included in it.

Report number two covers development and application of rapid sensors to determine bulk water chlorine and chloramine demand. It is useful to persons interested in water quality and chlorination/chloramination process control.

Report number three describes the methodology used and results obtained from a laboratory based evaluation to study to assess the performance of a number of commercially available online disinfectant residual analysers. It is useful to persons interested in measuring disinfectant residual online as well as evaluating and selecting online disinfectant residual analysers.

Report number four is a PhD thesis describing the development and evaluation of prototype software suite to optimise chemical disinfection control in two full scale distribution systems used as case studies to the project. The software includes an artificial neural network module. The study aims to develop control algorithms that can be used to predict disinfectant residual and chemical dosing requirements. The thesis will be of most value to persons interested in developing knowledge about ANNs.

Research Report Title: Development of Tools for Improved Disinfection Control Within Distribution Systems – Part 2 Development of a Surrogate Demand Sensor

Research Officers: Fiona Fitzgerald

Project Leader: Christopher Chow and Mike Holmes

Research Nodes:
Australian Water Quality Centre, Adelaide

CRC for Water Quality and Treatment Project No. 2.0.2.5.0.1 – Development of Tools for Improved Disinfection Control Within Distribution Systems
EXECUTIVE SUMMARY

This report describes the findings of a 12 month study to develop a “Disinfectant Demand Sensor”. The aim was to determine the 3 or 7 day demand of a water in less time. From our data we have produced the equation \( y = 1.86x + 0.82 \) with an \( R^2 \) value of 0.94 to predict the 3 day chlorine demand \( (y) \) from a 1 hour chlorine demand \( (x) \). In addition, the equation \( y = 2.31x + 1.19 \) with an \( R^2 \) value of 0.91 predicts the 7 day chlorine demand \( (y) \) from a 1 hour chlorine demand \( (x) \).

Water quality data (prior to disinfection) was used to identify surrogate parameters for disinfectant demand. The study found that the surrogate parameters of major interest were UV\textsubscript{254}, DOC, and colour with \( R^2 \) values of 0.91, 0.94 and 0.83 respectively.

Rapid fractionation of a water sample uses resins to separate the organic component into various fractions depending on chemical properties and the VHA fraction (humic acid fraction) shows the best relationship with disinfectant demand and so was also identified as a possible surrogate parameter for disinfectant demand with an \( R^2 \) value of 0.88.

The temperature investigation used the concept of raising the temperature of a sample thereby reducing the time taken to reach the 3-day demand equivalent. This study showed very promising results and this method of disinfectant demand prediction will be further developed in stage two of the project. For instance the 3 day chlorine/chloramine demand equivalents of Myponga Raw water can be determined after just 5.3 / 5.5 hours respectively when the sample is heated to 40°C.

The study has identified several methods of disinfectant prediction from surrogate parameters to temperature elevation. Chlorine demand could be linked with several surrogate parameters such as UV\textsubscript{254}, DOC, Colour, VHA and temperature to predict its demand in a shorter time.

Chloramine however, did not show the same relationship with the surrogate parameters but the temperature elevation technique could be used to effectively predict chloramine decay. A table summarising all the \( R^2 \) values is shown below:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>3 day chlorine demand</th>
<th>Predictability</th>
<th>3 day chloramine demand</th>
<th>Predictability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-hr demand</td>
<td>0.94 ( (0.91) )</td>
<td>Good</td>
<td>0.69 ( (0.60) )</td>
<td>Poor</td>
</tr>
<tr>
<td>3-hr demand</td>
<td>0.97 ( (0.95) )</td>
<td>Good</td>
<td>0.72 ( (0.63) )</td>
<td>Poor</td>
</tr>
<tr>
<td>6-hr demand</td>
<td>0.97 ( (0.95) )</td>
<td>Good</td>
<td>0.77 ( (0.68) )</td>
<td>Poor</td>
</tr>
<tr>
<td>3-day demand</td>
<td>(0.99)</td>
<td>Good</td>
<td>(0.90)</td>
<td>Good</td>
</tr>
<tr>
<td>Single Parameter</td>
<td>UV</td>
<td>0.94</td>
<td>Good</td>
<td>0.36 ( (0.60) )</td>
</tr>
<tr>
<td></td>
<td>DOC</td>
<td>0.91</td>
<td>Good</td>
<td>0.42 ( (0.63) )</td>
</tr>
<tr>
<td></td>
<td>Colour</td>
<td>0.83</td>
<td>Reasonable</td>
<td>0.35 ( (0.64) )</td>
</tr>
<tr>
<td></td>
<td>VHA</td>
<td>0.88</td>
<td>Reasonable</td>
<td>0.37 ( (0.65) )</td>
</tr>
<tr>
<td>Multiple Parameters</td>
<td>UV,DOC,Col,VHA</td>
<td>0.94</td>
<td>Good</td>
<td>0.45 ( (0.60) )</td>
</tr>
<tr>
<td></td>
<td>UV,DOC,Col</td>
<td>0.94</td>
<td>Good</td>
<td>0.45 ( (0.60) )</td>
</tr>
<tr>
<td></td>
<td>Col, UV</td>
<td>0.94</td>
<td>Good</td>
<td>0.44 ( (0.60) )</td>
</tr>
<tr>
<td></td>
<td>UV DOC</td>
<td>0.94</td>
<td>Good</td>
<td>0.43 ( (0.60) )</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>0.98</td>
<td>Good</td>
<td>0.98 ( (0.60) )</td>
</tr>
</tbody>
</table>
Additional investigations looked at High Performance Size Exclusion Chromatography (HPSEC), oxidation and reduction potential (ORP), and UV\textsubscript{272} in relation to disinfectant demand.

HPSEC was used to look at the organic character of the water with the intention of identifying the organic components responsible for the disinfectant demand. This method proved to be a useful tool for organic characterisation; however, its use in the prediction of disinfectant demand is limited at present.

ORP showed some promise as a surrogate parameter for disinfectant residual monitoring but requires further investigations to validate its use.

UV\textsubscript{272} was also studied and has shown promise as a monitoring technique for chlorine residual.

This report details the findings of this 12 months study and stage two of the project will further investigate their use as disinfectant demand sensors.
1 INTRODUCTION

CRCWQ&T Project 2.5.0.1. “Development of Tools for Improved Disinfection Control Within Distribution Systems”, has three components, Artificial Neural Networks (ANN) development (Adelaide University), assessment of currently available chlorine sensors (United Water International) and the development of a disinfectant demand sensor (Australian Water Quality Centre, AWQC). This report details the findings to date of the Disinfectant Demand Sensor component conducted by the AWQC. The aim of this component was to look at the possibility of designing a Disinfectant Demand Sensor which predicts disinfectant demand and which will hold over a range of water qualities.

The need for such a sensor arises from the fact that the biggest risk to public health when managing the supply of municipal potable water is the inadequate treatment of microbiologically contaminated water. The addition of a disinfectant and the maintenance of a residual in the distribution system help to ensure the destruction of organisms potentially infectious to humans. However, to maintain a residual it is necessary to have some idea of the disinfectant demand of the water and conventional measurement method is time consuming. A sample must be taken to the lab where it is dosed and allowed to decay for up to 7 days in order to find the disinfectant demand of that water, thus allowing operators to dose accurately to maintain a residual in the distribution system. The aim of this component is to try to determine that demand in a much shorter time by using either surrogate parameters, organic characterisation techniques or by physical means such as increased temperature.

Two disinfection methods commonly used are chlorination and monochloramination (the latter is applied by the addition of ammonia and chlorine compounds separately into a water pipe or tank). The application of chlorine as a disinfectant is simpler than chloramine but is highly reactive with natural organic matter (NOM) producing disinfection by-products (DBPs), and its decay is proportional to the dissolved organic carbon (DOC) concentration (Holmes et al., 2002). In contrast, chloramine is less reactive than free chlorine with NOM and this property makes it an attractive alternative secondary disinfectant to chlorine as it maintains a better disinfection residual and produces less DBPs (Vikesland et al, 1998).

As both disinfectants are chemically different, both were studied separately in the attempt to develop a demand sensor specific to each one.

This report describes the work carried out at the AWQC, South Australia to link disinfectant decay (chlorine/chloramine) with a number of parameters namely water quality, organic characterisation and temperature.
2 MATERIALS AND METHODS

Industry Partners provided 20 litres of raw and treated water (before chlorination) where applicable, once every three months from June 2003 to March 2004. From March 2004 to March 2005 a validation sampling programme will be conducted.

The selection of water includes:

Table 2.1: Industry Partner Samples

<table>
<thead>
<tr>
<th>Industry Partner Samples</th>
<th>Water Provider</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardinia Reservoir</td>
<td>Melbourne Water</td>
</tr>
<tr>
<td>Moondara Raw water</td>
<td>Gippsland Water</td>
</tr>
<tr>
<td>Moondara Treated water (Traralgon WTP)</td>
<td>Gippsland Water</td>
</tr>
<tr>
<td>Woronora Raw Water</td>
<td>Sydney Water</td>
</tr>
<tr>
<td>Woronora Treated Water</td>
<td>Sydney Water</td>
</tr>
<tr>
<td>Upper Hinze Dam</td>
<td>Gold Coast Water</td>
</tr>
<tr>
<td>Mudgeeraba WTP Treated Water</td>
<td>Gold Coast Water</td>
</tr>
<tr>
<td>Darwin River Dam Raw Water</td>
<td>Power and Water</td>
</tr>
<tr>
<td>Jandakot Raw Water (Bore Water)</td>
<td>Western Australia</td>
</tr>
<tr>
<td>Jandakot Treated Water</td>
<td>Western Australia</td>
</tr>
<tr>
<td>Morgan Raw Water (River Murray)</td>
<td>SA Water</td>
</tr>
<tr>
<td>Morgan Treated Water</td>
<td>SA Water</td>
</tr>
<tr>
<td>Happy Valley Raw water</td>
<td>United Water</td>
</tr>
<tr>
<td>Happy Valley Treated Water</td>
<td>United Water</td>
</tr>
<tr>
<td>Myponga Raw Water</td>
<td>United Water</td>
</tr>
<tr>
<td>Myponga Treated Water</td>
<td>United Water</td>
</tr>
</tbody>
</table>

The selection of waters listed above provided a wide range of water quality characteristics encompassing Australia and covered a DOC range of 1.5 mg/L to 13.5 mg/L. The selection of sampling sites allowed the entire country to be represented as illustrated in the following map (Figure 2.1).

Figure 2.1 Distribution of sampling sites around Australia

The 3-day chlorine demand (ClD) of each sample is shown on the graph below. This graph (Figure 2.2) not only illustrates the range of waters that were used in this study but also shows how ClD is related to the DOC content of the water. In the majority of cases the relationship between 3 day ClD and DOC is approximately a 1:1 ratio where 1mg/L DOC will consume 1mg/L chlorine. In the case of
Jandakot raw water however, this is a ground water sample with a very high iron content which would exert an additional inorganic demand.

Figure 2.2: DOC and 3-day Chlorine Demand for all Industry Partner samples.

In the analyses, each sample was chlorinated and chloraminated and a seven day decay was carried out at constant temperature (20°C) at 1, 3, 6, 24, 72 and 168 hour intervals. Chloramination was carried out at pH 8.2, ammonia was added first followed by chlorine while mixing. At each interval pH, $\text{UV}_{254}$ and oxidation-reduction potential (ORP) were recorded.

In addition, water quality parameters were measured, which include pH, DOC, TOC, $\text{UV}_{254}$, $\text{UV}_{272}$, Colour, Turbidity, Iron, Manganese, Bromide, Ammonia, Nitrite and Oxidation Reduction Potential (ORP). These were measured to establish any surrogate parameters for disinfectant demand, investigate any occurrence of inorganic chlorine demand and nitrification.

Organic characterisation in the form of HPSEC and Rapid Fractionation were also conducted. The methods for these analyses are found in the Appendix.

This data was collected over a year to include any seasonal variation which may occur. A second validation year is currently underway using a more refined experimental programme than the initial data collection programme. Currently a three day demand, DOC, $\text{UV}_{254}$, Colour, Rapid Fractionation (VHA fraction only) and HPSEC are conducted. These are the parameters that have shown the most promise as discussed later in this report, and is the design basis for the Demand Sensor currently undergoing trials.
3 RESULTS AND DISCUSSION

3.1 Chlorine

3.1.1 Chlorine Decay

In this study, chlorine decay was measured over 7 days for each sample at two different doses. What has been determined from the data produced from a seven day curve, is that it may not be necessary to wait until 7 days in order to find out the demand. The reason for this is that the three day demand correlated with seven days with an $R^2$ value of 0.99 (Figure 2.3a).

Figure 2.3 (a) 3 day vs 7 day ClD (b) 1hr vs 3 day ClD (c) 3hr vs 3 day ClD.

And furthermore, the 1 hour titration and 3 hour titration results correlated with the 3 day demand with an $R^2$ value of 0.94 and 0.97 respectively (Figure 2.3b and 2.3c). This means that a three day or seven day demand could potentially be determined in just 1 hour.

The following table shows how the 3 day or 7 day demands can be predicted by using the demand at say 1 hour, 3 hour or 6 hour demands. From the correlation graphs that produced the $R^2$ values below, an equation can easily be established using the best correlations available.
Table 2.2 $R^2$ values over chlorine decay curves

<table>
<thead>
<tr>
<th></th>
<th>3 days</th>
<th>7 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hr</td>
<td>0.94</td>
<td>0.91</td>
</tr>
<tr>
<td>3 hr</td>
<td>0.97</td>
<td>0.95</td>
</tr>
<tr>
<td>6 hr</td>
<td>0.97</td>
<td>0.95</td>
</tr>
<tr>
<td>3 days</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>7 days</td>
<td>0.99</td>
<td>-</td>
</tr>
</tbody>
</table>

From table 2.2, the 6 hour demand produces the best fit with both the 3 day and 7 day demands, so the equation to use for prediction is:

**For a three day demand prediction:**

$$y = 1.48x + 0.47$$

*Where:* $y = 3$ day demand  
$x = 6$hr demand

**For a seven day demand prediction:**

$$y = 1.7x + 0.76$$

*Where:* $y = 7$ day demand  
$x = 6$hr demand

### 3.1.2 Surrogate Parameters for Chlorine Demand

A range of water quality parameters were measured with the aim to find a suitable surrogate parameter for chlorine demand. The parameters included: pH, DOC, TOC, $\text{UV}_{254}$, $\text{UV}_{272}$, Colour, Turbidity, Iron, Manganese, Bromide, Ammonia, Nitrite and ORP.

The results have shown that DOC, $\text{UV}_{254}$, $\text{UV}_{272}$, and Colour are potential surrogate parameters for chlorine demand as illustrated in the graphs below. These findings hold over a wide range of samples and seasonal variations and are in keeping with Edzwald et al (1985) and Chang et al (1998). They have produced $R^2$ values of 0.91, 0.94, 0.84, and 0.83 respectively with the three day chlorine demand values as in Figure 2.4 (a), (b), (c), and (d). This means that using the equation of the graph, the chlorine demand may be determined by inserting the surrogate parameter value into the equation of the line. These graphs have been established using data from a 12 month period and using a wide range of samples, so in theory these surrogate parameter graphs could be universally applied.

In the demand sensor stage, this information will be used to predict chlorine demand using individual surrogate parameters and also a combination of these parameters as determined by a multi-linear regression analysis.
In addition, UV$_{254}$ can be used as a surrogate parameter for DOC as illustrated in the following graph. Edzwald et al (1985) explains that UV light is absorbed by conjugated double bonds and is a good technique for measuring NOM as humic substances contain aromatic moieties and are the dominant form of NOM in natural waters.

DOC is used as a measure of organic matter which is expressed as mg/L DOC.

As mentioned previously, other water quality parameters such as ammonia, bromide, iron, manganese, nitrite, redox potential and turbidity were measured but show poorer correlations with the chlorine demand than the previously mentioned parameters. The inorganic parameters were measured to take into consideration any additional chlorine demand they may produce, and nitrite was measured as an indicator of nitrification.

The only sample to show a significant inorganic input was Jandakot Raw with high iron levels ranging from 0.7 – 1.8 mg/L Fe over the 12 month study (Average value for all other samples was 0.18 mg/L Fe).
Jandakot raw water also had a high DOC (Range: 10.3 – 12.2 mg/L) and 3 day chlorine demand (Range: 12 – 30 mg/L). Treatment however effectively removed the majority of this iron leaving less than 0.1mg/L Fe.

3.1.3 Organic Characterisation

Organic characterisation was studied with the aim of understanding more about the organic matter component of water and its relationship with the chlorine demand.

By separating the organic matter into separate components based on charge and using rapid fractionation, it could be identified which of the fractions was mostly responsible for the uptake of chlorine. In addition, the HPSEC technique allows us to see differences in organic character based on molecular weight distribution between different sample locations and between raw and treated waters.

3.1.4 Rapid Fractionation

Rapid Fractionation (Chow et al., 2004) is the separation of organic matter using resins into different components according to their charge. The technique was based on the full-scale fractionation scheme reported by Croué et al. (1994) and Bolto et al. (1999). The fractions, in a broad categorisation, are split into VHA, (humic acids), SHA, (fulvic acids), CHA, (proteins, amino acids, and anionic polysaccharides) and NEU (carbohydrates, aldehydes, ketones and alcohols). It is generally thought that the humic acid fraction is responsible for the main uptake of chlorine (Afcharian et al, 1997), and from the results of our study, we have found this to be the case as shown below. The data used in the following graphs, was collected over 12 months from all the project partners and so includes any seasonal variation.

**Figure 2.6 VHA Fraction vs. 3 day Chlorine Demand**

Subsequent fractions produced poorer correlations with the 3 day chlorine demand as per Table 2.3.

**Table 2.3 Organic fractions vs correlation values**

<table>
<thead>
<tr>
<th>Fraction</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>VHA</td>
<td>0.88</td>
</tr>
<tr>
<td>SHA</td>
<td>0.66</td>
</tr>
<tr>
<td>CHA</td>
<td>0.41</td>
</tr>
<tr>
<td>NEU</td>
<td>0.05</td>
</tr>
</tbody>
</table>

However, SHA still produced a reasonable correlation with chlorine demand. For the purpose of chlorine prediction though, the VHA fraction should provide more accuracy. This indicates that by measuring the VHA content of a water sample the chlorine demand of that water may be predicted...
using the equation shown in Figure 2.6. This method takes considerably less time than conducting a complete chlorine decay curve.

The method of rapid fractionation requires DOC measurement of the sample before and after contact with the resin. A simple subtraction of these values gives the amount of DOC retained by the resin corresponding to the VHA fraction. As DOC measurement is a timely procedure, this study shows that UV$_{254}$ can act as a surrogate for DOC as in Figure 2.7, thus reducing even further the time taken to predict the chlorine demand (Figure 2.8). UV absorbance at 254nm is often used as a surrogate for DOC (Edzwald, 1993).

![Rapid Fractionation DOC vs UV$_{254}$](image1)

**Figure 2.7** DOC vs UV254 results from Rapid Fractionation

![Chlorine Demand vs VHA (UV254 cm$^{-1}$)](image2)

**Figure 2.8** Prediction of 3 day chlorine demand using UV254 of the VHA Fraction

The DOC concentration of the samples collected for this study ranged from approximately 1.6 mg/L to 13.0 mg/L. The results gained from the rapid fractionation technique showed the percentage of each organic fraction as in Table 2.4. This demonstrated that the application of the rapid fractionation technique could also be used to distinguish organic character in various water samples.
Table 2.4 Percentage range of fractions in Industry Partner samples

<table>
<thead>
<tr>
<th>Percentage Fraction of Total DOC</th>
<th>8 – 76%</th>
<th>11 – 28%</th>
<th>3 – 28%</th>
<th>8 – 49%</th>
</tr>
</thead>
<tbody>
<tr>
<td>VHA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SHA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NEU</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1.5 HPSEC

This method is used to show the molecular weight distribution of a sample and can be useful in the determination of chlorine demand. The graphs in the left column are the result of subtracting the treated water from the raw water curve. The graphs in the right column show the difference between the 3 day chlorine demand for the raw water and the treated water.

Plotting the peak height for each curve against the difference in chlorine demand (\(\Delta ClD\)) gives a good correlation with an \(R^2\) of 0.93. This shows that the area of the curve taken away by treatment is related to chlorine demand.

The HPSEC analysis is however, very time consuming and requires expensive instrumentation, and would therefore be considered impractical for the task at hand. However, while this method is not practical in the prediction of chlorine demand, it is a useful indication of the character of the organic constituent which is responsible for the uptake of chlorine. It could also be a useful tool in studying the efficiency of a water treatment method.
**Figure 2.9** HPSEC ∆Peak height and ∆CID of raw and treated samples.

**Figure 2.10** ∆Peak height vs ∆CID of raw and treated samples.
3.2 Chloramine

Chloramine is a much more complex and while it too is a disinfectant, that’s where its similarity with chlorine ends in terms of our work here. Results for this study have found that chloramine demand (NH₂ClD) does not correlate as well as free chlorine with the typical surrogate parameters for NOM as indicated by the following R-squared values.

Table 2.5 R² values for NH₂ClD vs Surrogate Parameters for NOM.

<table>
<thead>
<tr>
<th>Water Quality Parameter</th>
<th>R² value</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>0.47</td>
</tr>
<tr>
<td>UV₂₅₄</td>
<td>0.43</td>
</tr>
<tr>
<td>Colour</td>
<td>0.35</td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.00</td>
</tr>
</tbody>
</table>

To explain this, chloramine demand has been found to be independent of organic character as the following graph indicates. This rules out the use of DOC, UV absorbance and colour for chloramine prediction, which are all indicators of organic character.

Figure 2.11 Chloramine Demand is independent of organic character

In addition, chloramine did not perform well with the rapid fractionation method. The following graph illustrates the correlation of the 3 day monochloramine demand with the VHA fraction of each sample.

Figure 2.12 VHA Fraction vs Chloramine Demand
The correlation value is very poor showing that no real relationship exists between monochloramine and the VHA fraction. In addition, the rest of the fractions also correlate poorly with the 3 day monochloramine demand as in Table 2.6.

Table 2.6 Organic Fractions vs 3 day monochloramine demand

<table>
<thead>
<tr>
<th>Fraction</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VHA</td>
<td>0.37</td>
</tr>
<tr>
<td>SHA</td>
<td>0.43</td>
</tr>
<tr>
<td>CHA</td>
<td>0.23</td>
</tr>
<tr>
<td>NEU</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Due to the fact that chloramine demand is independent of organic character, all of the above options for disinfectant demand cannot be considered. However, one method for prediction did show promise for chloramine and this was the effect of increasing temperature as discussed in the following section.

3.3 Temperature Study

The effect of increasing the sample temperature on the time taken to reach the 3 day disinfectant demand equivalent was studied. Water samples from South Australia were used for this investigation and both raw and treated water samples were taken. Decays were set up at 20, 30, 40, and 50°C which allowed a calibration curve to be established for that water.

This study showed very promising results for both chlorine and chloramine as indicated in the graphs below. The results show that by elevating the temperature of a sample then dosing with disinfectant, the three day equivalent can be determined in a matter of hours, instead of waiting for three days.

Figure 2.13 Temperature Calibration Curves for Myponga Raw and Treated

For example, in the case of Myponga Raw Water - Chlorine, from the graph shown above the three day demand can be reached in just 5.25 hours (Ln 1.65) when the sample is heated to 40°C. The same applies to the chloramine prediction for Myponga Raw Water - Chloramine where the three day demand equivalent can be determine in just 5.5 hours (Ln 1.7) when the sample is heated to 40°C.
For this particular method of disinfectant prediction, a calibration curve needs to be established for the water in question. It has not been tested for seasonal variation as yet, but it may be assumed that it is a temperature dependent relationship and is not affected by any variations in organic matter. Further tests on a range of waters having differing chemical characteristics are required to confirm this test as a generic disinfectant demand surrogate.
4 ADDITIONAL INVESTIGATIONS

4.1 Oxidation Reduction Potential (ORP)

ORP was also studied whereby the ORP was measured at each titration point of the seven day decay. The aim was to see if ORP could be used as a surrogate parameter for chlorine residual. The use of ORP as a surrogate for chlorine residual and demand has been reported before by Yu and Cheng, (2003) and Sydney Water, (2000). ORP values fall in the region of 700-900 mV for chlorinated water and for chloraminated water the reading was always lower in the range of 400-600 mV. The results from this component were, however, inconsistent. When the ORP was correlated with the corresponding chlorine/chloramine residuals of a seven day curve, the correlation values for the entire set of Partner samples could range from an $R^2$ of 1 to no correlation at all.

Each time a sample was analysed the probe was inserted into the sample and allowed to equilibrate before taking a reading; however, it is thought that the results would be more consistent if the probe was kept in a sample continuously over the 7 day decay to ensure constant equilibration. This method was not possible with the number of samples being analysed but will be further investigated in stage 2 of the project.

4.2 UV$_{254}$ and UV$_{272}$

In addition to ORP at each titration point, UV$_{254}$ was also measured and this correlated well with the chlorine residual values over the 7 day decays further supporting its use as a surrogate parameter. The following graph illustrates the relationship between UV$_{254}$ and the chlorine residual at each point on the decay curve. A random sample has been taken as an illustration.

![Gold Coast Raw Chlorine Decay](image1)

**Figure 2.14** Potential to use UV$_{254}$ to monitor chlorine residuals.

From the decay curves for chloramine, it was also found that UV$_{254}$ could monitor the decay rate of chloramine but not predict its demand. An example of one particular 7 day decay is shown in Figure 2.15.

![Moondara Raw Monochloramine Decay](image2)

**Figure 2.15** Use of UV$_{254}$ to monitor monochloramine decay.
This method of monitoring monochloramine decay is similar to the use of $\text{UV}_{272}$ for monitoring chlorine decay as illustrated in the following graphs.

**Figure 2.16** Use of UV272 to monitor chlorine decay.

**Figure 2.17** Chlorine residual vs. UV272

Monitoring $\text{UV}_{254}$ and $\text{UV}_{272}$ can allow the monitoring of trends for both monochloramine and chlorine residuals respectively. However, as previously discussed $\text{UV}_{254}$ of the non-chloraminated sample cannot be used in the prediction of monochloramine demands. However, $\text{UV}_{254}$ can be used to predict the chlorine demand of a water as previously discussed in section 1 of this report.
5 CASE STUDIES

Two case studies were selected to demonstrate the chlorine demand sensor concept.

5.1 Myponga water treatment plant

A two week field trial using the S::CAN Spectro::lyser™ was conducted at the Myponga WTP (chlorinated system). The S::CAN Spectro::lyser™ was installed at the filtered water tap (prior to chlorination) at the WTP laboratory. A chlorine demand prediction algorithm based on previous laboratory data was used to determine the real time chlorine demand of the filtered water. During the two week field trial, 19 grab samples were taken for laboratory chlorine demand measurement. In addition, field chlorine residuals from the routine sampling program at a downstream location (Almond Grove Road – location number 1607) were used to evaluate the concept of “chlorine demand sensor” as a real time control of chlorine dosing. In terms of practicality, chlorine demand can also be estimated based on the difference between the chlorine set-point at the WTP and the residual at the downstream locations provided the water travel time is known.

A particularly useful feature of the S::CAN Spectro::lyser™ is the on-line / in-situ monitoring capability. During the 2-week on-line monitoring trial conducted at the Myponga WTP, the S::CAN Spectro::lyser™ performed well, with incorporation of specifically developed software. On-line chlorine demand prediction based on UV absorbance measurement was able to be displayed in real time on the instrument (Figure 2.18). The chlorine demand predictions matched well with the laboratory measurements made of grab samples collected during the period. Note that grab sampling did not occur during events of major changes in chlorine demand as detected by the S::CAN Spectro::lyser™ caused by plant shutdowns. This indicates that a sampling program can be refined using a S::CAN Spectro::lyser™ to enable samples to be taken when water quality changes or events occur rather than on a time, flow or random basis.

![Figure 2.18](image_url)

**Figure 2.18** Comparison of real time chlorine demand monitoring using on-line UV absorbance measurement and chlorine demand determined in a laboratory using conventional method.

Pink line: on-line chlorine demand prediction by S::CAN Spectro::lyser™. ○: Laboratory chlorine demand measurement from grab samples. ●: Determined chlorine demand based on chlorine residual at a location (Almond Grove Road – location number 1607) downstream from the Myponga WTP with travel time correction.

Furthermore, the “chlorine demand sensor” concept was studied using chlorine residual measurement at a location (Almond Grove Road) downstream of the WTP. The feasibility of using UV absorbance measurement (prior to chlorination) to estimate chlorine demand of the water as a way to control...
chlorine dosing and manage residual in the distribution system was assessed. The chlorine demand (field data) shown in Figure 2.18 was estimated based on the difference between the chlorine set-point at the WTP and chlorine residual at the Almond Grove Road sampling point after travel time correction (travel time is approximately 2 days), the results also matched well with the real time chlorine demand measurements using the S::CAN Spectro::lyser™. Although this study didn’t provide a full demonstration of using on-line UV spectrophotometer for chlorine dosing control, the results obtained so far indicate feasibility of the concept. More case studies are required to confirm the practicality of this control concept. A new project in the CRC for Water Quality and Treatment is currently underway to evaluate the S::CAN Spectro::lyser™ in a range of drinking water related projects.

5.2 Woronora Water Filtration Plant

Woronora is a chloraminated system – at WFP chlorine before ammonia. Below is an example of identifying the cause of water quality change at the WFP by monitoring the treated water quality (WFP outlet). During the monitoring period a very small spike (reduction of UVabs signal / calculated DOC) was observed, this probably was not notifiable with normal operational monitoring. By inspecting the derivative spectra as described previously, a spectral shift was clearly identified (Figure 2.19). The derivative spectrum at the spike occurred was a standout from the others, with the additional on-line data, it was noted that the WFP water flow was reduced during that period. The reduction of UV254 signal generally refers to the reduction of DOC / chlorine demand and the chlorine dosing system would automatically adjust the dose via a feedback control loop based on chlorine residual at the outlet.

![Figure 2.19 Illustration of the advantage of using UV/Vis-spectrometer for feed-forward control of the chlorine dosing system at the WFP.](image)

From the chlorine dosing record, the chlorine dose was also automatically reduced, however, this also showed the chlorine demand prediction algorithm detected the change 20 min ahead compared with the conventional feedback control. This also demonstrated that the potential application of using the UV/Vis-spectrometer signal for feed-forward control of the chlorine dosing system. The response of the control can be improved over the current feed back control based on the chlorine residual at the storage tank.
6 CONCLUSIONS

Having looked at two commonly used disinfectants in this study, chlorine and chloramine, it is clear that both are very different and it is not possible to apply the same sensor to both disinfectants in all our possible sensor options.

The surrogate parameters look extremely promising for chlorine prediction and the next phase of the project is to use these surrogate parameters in a test rig trial either individually or in combination using a multi-linear regression. The VHA option is also promising and could be used a potential surrogate sensor. A wide range of samples taken over an entire year have formed an extensive database incorporating any seasonal changes, for use in stage two of this study. As a result, the findings from the surrogate parameter study should allow any sample to be taken at any time of the year, providing us with a universal chlorine demand prediction tool.

The chloramine sensor has proved a little more difficult to establish, however the increased temperature option has shown great potential for both chlorine and chloramine. The results from this 12 month study seem to indicate that the decay of chloramine is independent of organic character, and so all surrogates and rapid fractionation options are not viable.

The two case studies have demonstrated and confirmed the chlorine demand sensor concept using an on-line UV spectrophotometer (S::CAN) in two treatment plant. The results were promising and a new CRC Water Quality and Treatment project has started to evaluate the benefits of using on-line water quality monitoring tools for the drinking water industry.
7 ACKNOWLEDGMENTS

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8 REFERENCES


DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

9 FURTHER INFORMATION

Project related publications


APPENDIX I

Methods

Determination of Chlorine and Monochloramine
Chlorine and chloramine residuals were determined using the FAS/DPD titrimetric method (APHA, 1998). The parameter measured is chlorine residual (both free and combined). The addition of potassium iodide solution catalytically causes monochloramine to produce colour. The colour change in this titration is from red to colourless.

Free chlorine, chloramine species and total chlorine in potable waters can be determined by this method in the range of 0.03mg/L to 5mg/L total chlorine and at higher concentrations by dilution of samples.

Chlorination of samples was carried out using a chlorine stock solution. This was prepared using compressed chlorine gas dissolved in MilliQ water. The concentration was determined before each use using the FAS/DPD titration method.

Chloramination was conducted at pH 8.2, using a chlorine to ammonia ratio of 4.5:1. Ammonia was added first, then chlorine while mixing.

pH/ORP
This was carried out using a Horiba (Model D-21 pH meter and probe, and Model D-22 pH meter and ORP probe).
Calibration of the ORP probe was not required, and for pH calibration BDH Buffers 4 and 7 were used in accordance with the operating instructions.

Rapid Fractionation
Rapid Fractionation is a method whereby the organic component of a water sample is separated into its individual organic fractions by passing through a resin. This allows the determination of four organic fractions, VHA, (adsorbed by DAX-8), SHA, (adsorbed by XAD-4), CHA, (adsorbed by IRA-958) and NEU, and the method has been published elsewhere (Chow et al., 2004).

Dissolved Organic Carbon Analysis
DOC concentrations were determined using a total organic carbon analyser (Model 820, Sievers Instruments Inc., USA).

UV absorbance
The absorbance at 254 nm was measured using a UV/VIS spectrophotometer (Model 918, GBC Scientific Equipment Ltd., Australia) with a 1 cm quartz cell.

Apparent Molecular Weight Determination
The high performance size exclusion chromatography (HPSEC) analysis was based on the method described by Chin et al. (1994). HPSEC was performed using a Waters 501 pump, 717 autosampler, 484 tunable UV detector, an Inter Action column oven set at 30°C and a Showa Denko, Shodex KW-802.5 packed column (Shoko Co. Ltd., Japan). The carrier solvent consisted of a 0.02 M phosphate buffer solution (pH 6.8) adjusted to an ionic strength of 0.1 M with sodium chloride. The flow rate was 1mL/min and the absorbance at 260 nm was measured. Calibration was performed using polystyrene sulfonate (PSS) standards (Polysciences Inc., U.S.A.) of molecular weights 35,000, 18,000, 8,000 and 4,600 daltons.

Colour
Colour was determined spectrophotometrically by comparing the absorbance of a sample at 456 nm with a platinum/cobalt standard (50 Hazen Units) (Bennett and Drikas, 1993) using a GBC UV/VIS 918 spectrophotometer (GBC Scientific Equipment Ltd., Australia).

Turbidity
A Hach 18900 ratio turbidimeter (Hach, U.S.A.) was used to give a direct reading of the turbidity of a sample in nephelometric turbidity units (NTU).
Manganese, Ammonia and Iron
These parameters were initially measured using Hach Test Kits which compared a colour change against a colour wheel. The kits were later upgraded to the Hach DR890 Colorimeter multi parameter unit and the analyses conducted using the appropriate reagent sets.

TOC and Bromide
These parameters were measured by the commercial laboratories at the Australian Water Quality Centre. Bromide was measured by ICP-MS, and TOC by the Beckman 915B TOC Analyser using the combustion - infrared technique.

S::CAN Spectro::lyser™
The S::CAN Spectro::lyser™ hardware is different in that rather than bringing the sample to the unit, the unit is submersible and can go directly into the water. It comprises a robust but sensitive double beam UV/Vis-spectrometer (200nm to 750nm) with optical path length in a selectable range of 0.05 to 10 cm. The instrument was designed based upon the principle of the photodiode array (PDA) spectrophotometer, which has no moving parts and has the advantage of reagent free operation. Full spectrum UV/Vis absorbance measurement provides concentration data for a number of parameters and calculated equivalents for others (such as TOC, DOC, nitrate, nitrite, turbidity, total suspended solids and particle size). It has proved to be a useful warning tool of any sudden changes of water quality. Consequently the S::CAN Spectro::lyser™ has many diverse applications, including monitoring of drinking water, domestic and industrial waste waters.
APPENDIX II

Disinfectant demand prediction using surrogate parameters – a tool to improve disinfection control

Fiona Fitzgerald, Christopher W. K. Chow and Michael Holmes

ABSTRACT

This paper describes the findings of a study to develop a "Disinfectant Demand Sensor". The aim was to determine the 3- or 7-day demand of a water sample in a shorter period of time, such as a few hours. Three approaches were taken to achieve this: (a) assessment of water quality surrogate parameters, (b) "short" disinfection demand assessment, and (c) temperature elevation approaches. All these methods can be used for the prediction of chlorine, but only temperature elevation and short demand assessment can be used for the prediction of chloramine with good accuracy.

Water quality data (prior to disinfection) was used to identify surrogate water quality parameters for disinfectant demand. The study found that the surrogate parameters of major interest were UV254, DOC, and colour with $R^2$ values of 0.94, 0.91 and 0.83, respectively for chlorine demand prediction.

A rapid fractionation technique using ion-exchange resins to separate the organic component into various fractions demonstrated that the VHA (Very Hydrophobic Acidic/humic acid) fraction showed the best relationship with chlorine demand and was also identified as a possible surrogate parameter with an $R^2$ value of 0.88. Chloramine demand did not behave similarly. Other factors influencing chloramine decay make it more difficult to predict than chlorine decay.

The possibility of using the demand of a shorter time span to predict demands of a longer time was also investigated. This technique was proved to work well for both chlorine and chloramine and results have shown that a 3-h chlorine demand correlated well with the 3-d demand ($R^2 = 0.97$). Also, the 1-d chloramine demand correlates with the 3-d demand ($R^2 = 0.92$).

Thirdly, the temperature investigation used the concept of raising the temperature of a sample thereby reducing the time taken to reach the 3-d demand equivalent. This method was found to be suitable for both chlorine and chloramine demand prediction. For example the 3-d chlorine/chloramine demand at 20°C equivalents of Myponga water can be determined after just 5.3/5.5h respectively when the sample is incubated at 40°C.

Key words | chloramine, chlorine, demand prediction, disinfection, water quality

INTRODUCTION

The goal of most water quality managers is to maintain a safe water supply that is palatable to customers. Maintaining a disinfectant residual throughout the distribution system is an effective way of ensuring the aesthetic and bacteriological quality of the water at the customer tap. Chlorine is one of the most widely used disinfectants in drinking water treatment. The benefits of chlorine disinfection are well known and include low cost, a broad range of effectiveness and it has the added advantage of remaining active within the system for a considerable time. However, because of its ability to produce odours, the concentrations of chlorine and particularly the variability of
these concentrations is one of the most frequent causes of customer complaints. The conditions in Australia make control of disinfectant residual in distribution systems difficult. Problems arise from high levels of natural organic matter (NOM) that result in a high disinfectant demand, seasonal variation in flow demands and varying water temperatures. In addition, distribution systems are designed primarily for supply and fire fighting rather than optimised for water quality and hence long residence times may be found in water storage tanks and distribution pipelines. Monitoring of disinfectant residual in the water distribution system often suffers from delayed feedback which results in reduced responsiveness in disinfectant dose changes at the treatment plant. Consequently, applied doses that are either too high or too low are often identified too late for an operator to react and to take corrective action (Hua et al. 1999; Rodriguez & Serodes 1999).

Downstream of the treatment plant, chlorine gradually dissipates in the distribution system due to the reactions between various organic and inorganic compounds. The consumption of residual chlorine in the distribution system is influenced by: (1) bulk water reactions with organic and inorganic chemicals; (2) reactions with biofilms attached to the distribution pipe wall; (3) reactions between chlorine and corrosion deposits; and (4) mass transport of chlorine and other reactants between the bulk flow and pipe wall (Jadas-Hecart et al. 1993; AWWA 1996; Vasconcelos et al. 1997). Generally these can be considered as chlorine decay in the bulk water and due to surface reaction (Kiene et al. 1998; Kastl et al. 1999b). Bulk chlorine decay rates due to chemical reactions in the aqueous phase can further be separated into fast and slow reactions. Fast reactions take place with easily oxidisable compounds such as inorganic compounds and are usually completed during primary disinfection at the treatment plant. Slow reactions proceed with less oxidisable compounds such as NOM (Dotson & Heltz 1995; Jadas-Hecart et al. 1993; Kastl et al. 1999a, 1999b; Powell et al. 2000) and may occur in the distribution system. The bulk chlorine decay rates have also been observed to increase with temperature (Jadas-Hecart et al. 1993).

Conventional bulk water disinfectant demand methods are contact time dependent and often require several days to complete in order to match actual water ages found in water distribution systems. Knowledge of the bulk water chlorine or chloramine demand is useful for a number of reasons. It can be used to assess water quality and to assist managers in optimising primary as well as secondary disinfection. It must also be determined in order to provide calibration constants if hydraulic models are to be used to predict disinfectant residuals in distribution systems.

In some cases, water quality prior to disinfection can vary markedly. Changes may be gradual, in the case of seasonal variation, or rapid if water is supplied from a number of sources. Unstable water supplies, having variable water quality, may exert a variable disinfectant demand. This requires substantial changes to be made to the applied disinfectant dose if disinfection residuals are to be maintained within the required ranges throughout the disinfection system. This presents a challenge to operators when attempting to control secondary disinfection as feedback loops are usually of the order of several days, making the process highly reactive.

This paper reports the suitability of a number of water quality parameters which were investigated as potential surrogates for disinfectant demand prediction. These will be utilised for the development of a rapid, on-line and generic "Disinfectant Demand Sensor" which can be used for a range of water qualities. The approach of this research was to formulate a relationship between the measurable surrogate parameters and disinfectant demand measured using the conventional methods over a set of water samples with a wide range of water quality. The main body of this study involved sample collection once every three months over a one year period to obtain waters from around Australia. The water quality including organic characterisation and disinfection decays of these samples were determined. Relationships between the disinfectant demand and these water quality parameters were established in order to identify surrogate parameters for both chlorine and chloramine.

Apart from using the measurable water quality parameters to predict long term demand (eg. 5- or 7-day), two other approaches, using the disinfection demand of a shorter time (3-h) and elevating the temperature of a sample to above ambient level, were evaluated. The temperature elevation study was conducted to determine the feasibility of raising the temperature of a disinfected sample to decrease the time taken to reach the 3-d demand equivalent at ambient temperature. These approaches
provided three potential techniques of disinfection demand prediction.

**EXPERIMENTAL**

**Sampling locations**

Water samples from different locations in Australia, including New South Wales (NSW), Northern Territory (NT), Queensland (QLD), South Australia (SA), Victoria (VIC) and Western Australia (WA), were selected for this study. The water collection program was designed to collect a batch of 16 samples, comprising both raw and treated waters, from the selected locations every three months between 2003 and 2004. This selection produced a database of varying water qualities throughout Australia and incorporated seasonal variation. The database facilitated the determination of surrogate parameters for the prediction of disinfection demand that would hold over a range of water qualities and seasons.

**Analytical methods**

General water quality parameters, pH (D-21 and 982010D, Horiba, Japan), turbidity (2100AN, Hach, USA) and dissolved organic carbon (DOC) (820, Sievers Instruments Inc., USA) and UV absorbance at 254 nm (UV254) (Model 918, GBC Scientific Equipment Ltd., Australia) were determined using the methods described in Standard Methods (APHA 1998). Colour was determined using the spectrophotometric method described in Bennett & Drilicas (1993). Ultrapure water used in these experiments was obtained from a Milli-Q® purification system (Millipore, France).

The rapid organic fractionation technique reported in Chow et al. (2004b) was modified just for the determination of the very hydrophobic acids (VHA) fraction (adsorbed by DAX-8).

Chlorine decay was determined by dosing an appropriate volume of saturated chlorine solution into the samples with pH adjusted to 7.2. For chloramination (monochloramine), ammonia then chlorine was added at a ratio of 4.5:1 = \( \text{Cl}_2: \text{NH}_3 \) at pH 8.2 while mixing. Sample size was 2 litres and was stored in an amber bottle at 20°C ± 2°C. At predetermined times 100 mL samples were taken for chlorine/chloramine analysis over a period of 7 d. Chlorine residual was determined using the N.N-diethyl-p-phenylenediamine (DPD) titration method. DPD is used as an indicator in the titration procedure with ferrous ammonium sulfate (FAS) (APHA 1998). Chloramine residual was determined after the addition of a few drops of 5% potassium iodide solution (APHA 1998). For other decay temperatures (temperature evaluation study), a water bath with variable temperature control (Reciprocating Shaking Water Bath Model RW 1812, Paton Science Pty Ltd, Australia) was used.

**RESULTS AND DISCUSSION**

**Sample selection**

The water samples investigated in this study provided a wide range of water quality characteristics found in Australia and covered a DOC concentration range of 1.5–13.5 mg/L. The selection of the 16 sample batches was based on an earlier screening test (Chow et al. 2004b), which contained over 35 water samples. A summary of general water quality parameters, DOC, UV254, and colour are presented in Table 1.

Treatment of some supplies consisted simply of disinfection while others used several clarification processes including coagulation/flocculation-sedimentation-filtration prior to disinfection. For those waters requiring treatment prior to disinfection (coagulation-sedimentation-filtration), both the raw and treated waters were included, whereas for water sources without the need of a clarification process, only raw water was used. The reason for using raw water was to provide a larger variation in water quality. All waters used for this study were collected before disinfection.

**Demand prediction using water quality parameters**

NOM is usually represented by the measurement of total (TOC) or DOC concentration. The impact of NOM on various treatment processes is based upon both
concentration and character (Owen et al. 1995). Characterisation techniques, such as fractionation using resins and structural analysis using analytical instrumentation, have been developed worldwide to study the character of NOM. In particular, UV$_{254}$ is one of the simplest methods and is widely adopted by the water industry. It has been reported as a surrogate parameter to monitor the concentration of NOM (Edzwald et al. 1985; Wang & Hsieh 2000). In addition, UV$_{254}$ tends to give a measure of unsaturated organic bonds, which are potential sites with which chlorine can react. The UV absorbance of NOM in a water sample is potentially related to its chlorine demand (Powell et al. 2000). It can also provide a measure of overall disinfection by-product formation after chlorination (Korshin et al. 1997; Li et al. 1998).

**Single parameter prediction**

Three general water quality parameters, DOC, UV$_{254}$ and colour, were examined individually and correlated well with the 3-d chlorine demand; DOC ($R^2 = 0.91$), UV$_{254}$ ($R^2 = 0.94$) and colour ($R^2 = 0.83$), as shown in Figure 1(a). The results have confirmed that a relationship exists between chlorine demand and the parameters DOC, UV$_{254}$ and colour. These parameters are potential surrogates for chlorine demand and, by using the regression equation of the graph, the chlorine demand may be determined by inserting the surrogate value into the equation of the line.

Figure 1(b) shows the predicted versus actual 3-d chlorine demand using the corresponding water quality parameters. These graphs have been established using data from a 12 month period and using a wide range of samples, so in theory these surrogate parameter graphs could be applied nationally. In addition, these findings hold over a wide range of samples and seasonal variations and are in keeping with Edzwald et al. (1985) and Chang et al. (1998).

NOM is a well known factor that can impact on chlorination and chloramination. The use of simple water quality parameters such as DOC, UV$_{254}$ and colour can provide some information about the organics. The application of an organic characterisation technique is a useful tool to obtain more detailed information on the NOM. However, most of the organic characterisation techniques are generally time consuming and rely heavily on very sophisticated instrumentation, which makes these techniques unsuitable for rapid assessment. However, a rapid fractionation method based on the selective adsorption of organic compounds with different chemical properties onto specific types of ion-exchange resin has been reported (Chow et al. 2004a). A further simplified version which determines just the VHA fraction was used to assess the predictability of disinfectant demand. The VHA fraction of organic matter, which is sometimes attributed to the humic acid fraction, showed the strongest correlation to the 3-d chlorine demand and so can be used in its prediction.

A complete set of regression analyses is presented in Table 2 with $R^2$ values of the correlation between water quality parameters against 1-h, 3-h, 6-h, 1-d, 3-d and 7-d chlorine demand. The results indicate that the water quality parameters correlate strongly with each step of the chlorine decay curve with the highest correlation being achieved for UV$_{254}$ ($R^2 = 0.94$), DOC ($R^2 = 0.91$), VHA ($R^2 = 0.88$) and colour ($R^2 = 0.83$) with the 3-d demand prediction.

These $R^2$ values show that it is not necessary to measure all three parameters to correlate water quality with chlorine demand. This is logical, given that UV$_{254}$, DOC and colour are generally understood to be interrelated.

In Figure 1(b), the plots of predicted versus actual chlorine demand using these parameters indicate a linear relationship and confirm that a reasonable prediction can be established. However, this general equation (including both raw and treated waters) may not be able to provide the required accuracy for water quality managers to predict chlorine demand. Statistical analysis by using UV$_{254}$ of just
the treated waters has confirmed that this fine-tuned equation has a prediction accuracy of better than ±1 mg/L chlorine demand (Figure 2). The data used to establish this relationship were analysed and outliers removed. The outliers were found to be consistently from two particular sources of water. One of the sources had ammonia present in the treated water prior to chlorination.

The presence of ammonia can impact on chlorine demand prediction as it reacts with chlorine to form chloramine. In order to get reliable chlorine demand prediction from $UV_{254}$, DOC or colour, it is worth checking the water is ammonia free.

Similar experiments were conducted for chloramination. Chloramine demand did not correlate well with the measured parameters; for example $UV_{254}$ ($R^2 = 0.42$), colour ($R^2 = 0.39$) and DOC ($R^2 = 0.40$) for the 3-d...
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

Figure 2 | (a) The refined relationship between UV absorbance at 254 nm and 3-d chlorine demand. (b) The predicted 3-d chlorine demand using UV absorbance at 254 nm versus the actual 3-d chlorine demand. The dotted lines represent ±1 mg/L chlorine demand boundary.

demand prediction (Table 3). Unlike chlorine demand correlation (Table 2), it appears that the chloramine correlation ($R^2$) is in the order of VHA > DOC > colour > UV254 (Table 3). The mechanism of chloramine decay is certainly more complex compared with chlorine decay (Leung & Valentine 1994a,b; Vitek et al. 2007; Duirka et al. 2005). A recent publication by Duirka et al. (2005) has confirmed there are two reaction pathways, monochloramine autodecomposition and reaction with NOM, which is rather complicated for monochloramine decay in the presence of NOM. Further work needs to be focused on selecting alternative analytical techniques to identify the parameters related to chloramine decay.

Multiple parameters

Instead of confining the prediction of disinfection demand to just a single surrogate parameter, a combination of the surrogate parameters can be used to predict chlorine. A multi-linear regression analysis using Excel’s Data Analysis Toolbox (Microsoft, USA) allowed different combinations of surrogate parameters to predict chlorine demand.

Table 3 | The $R^2$ values of the correlation study of each water quality parameter against chlorine demand.

<table>
<thead>
<tr>
<th>Chloramine demand</th>
<th>DOC</th>
<th>UV254</th>
<th>Colour</th>
<th>VHA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-h</td>
<td>0.20</td>
<td>0.18</td>
<td>0.23</td>
<td>0.22</td>
</tr>
<tr>
<td>3-h</td>
<td>0.23</td>
<td>0.20</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>6-h</td>
<td>0.25</td>
<td>0.22</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>1-d</td>
<td>0.35</td>
<td>0.31</td>
<td>0.35</td>
<td>0.40</td>
</tr>
<tr>
<td>3-d</td>
<td>0.42</td>
<td>0.36</td>
<td>0.34</td>
<td>0.45</td>
</tr>
<tr>
<td>7-d</td>
<td>0.48</td>
<td>0.42</td>
<td>0.39</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Table 4 | Multiple regression analysis for chlorine demand prediction

<table>
<thead>
<tr>
<th>Parameter combination</th>
<th>3-d demand</th>
<th>7-d demand</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV254, DOC, colour, VHA</td>
<td>0.95</td>
<td>0.94</td>
</tr>
<tr>
<td>UV254, DOC, colour</td>
<td>0.95</td>
<td>0.94</td>
</tr>
<tr>
<td>Colour, UV254</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>UV254, DOC</td>
<td>0.95</td>
<td>0.94</td>
</tr>
<tr>
<td>DOC, colour</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td>UV254</td>
<td>0.94</td>
<td>0.94</td>
</tr>
</tbody>
</table>
From the correlation results shown in Table 4, marginal improvement based on the $R^2$ value can be obtained by using multiple parameters. However, it can be concluded that not all parameters contribute to an accurate prediction to the same degree as simply measuring UV$_{254}$ produces almost the same correlation as using all four parameters.

**Short demand assessment to predict longer decay**

White (1992) has reported a mathematical equation to predict chlorine demand at the end of any contact time, providing the chlorine demands at 1 h and at 30 min are known. In this part of the study, the concept of using short demand values to predict longer demand values is extended to samples with a wide range of water quality. Disinfectant decay curves were established over a duration of 7 d in this study with demands taken at 1, 3, 6, 24, 72 and 168 h. It was investigated if the determination of a 1-, 3- or 6-h disinfection demand could lead to the prediction of longer demand times such as multiple days. A simple regression analysis was performed by plotting the shorter demand against longer demand. A graph of 3-h chlorine demand against 3-d chlorine demand has shown that the 3-h results correlated with the 3-d demand with an $R^2$ value of 0.97 (Figure 3(a)). This confirmed that it is feasible to use a shorter demand to predict the demand after several days.

A detailed regression analysis is presented in Table 5. A similar analysis was performed on chloramine decay and the results showed some potential for predicting 3- and 7-d demand using a shorter contact time demand. The most promising prediction was found using 1-d demand to predict 3-d demand ($R^2 = 0.92$).

**Temperature elevation approach**

Temperature is an important factor that influences chlorine and chloramine decay. In this study, an attempt was made to take advantage of the fact that at higher temperatures disinfectant will decay faster. Understanding of this can also be used to predict decay caused by diurnal temperature fluctuations. In many parts of Australia, temperature variation can be very large (temperature can reach 45°C in mid-afternoon) which can have a significant impact on disinfectant residual control.

The effect of increasing the sample temperature on the time taken to reach the 3-d disinfectant demand equivalent was studied. Water samples from South Australia were used for this investigation and both raw and treated water samples were taken. Decays were set up at 20, 30, 40, and 50°C which allowed a calibration curve to be established for that water as shown in Figure 4.

This study showed very promising results for both chlorine and chloramine, as indicated in the graphs. The results show...
that by elevating the temperature of a sample then dosing with disinfectant, a 3-d equivalent can be determined in a matter of hours, instead of waiting for three days.

For example, in the case of chlorine, Figure 4(a) shows the 3-d demand (ambient temperature 20°C) can be reached in just 5.25 h (log, 1.65) when the sample is heated to 40°C. The same applies to the chloramine prediction for Myponga Water – Chloramine where the 3-d demand equivalent can be determine in just 5.5 h (log, 1.7) when the sample is heated to 40°C.

Further validation work was carried out to test this approach for both chlorine and chloramine. Using the above calibration curves, the samples were heated and the demands were determined at the times indicated. Figure 5 shows a range of actual chlorine and chloramine demand results plotted against the values obtained at a higher temperature and shorter reaction time. This illustrates the feasibility of this approach for both chlorine and chloramine.

It was established for this particular method of disinfectant prediction that an individual calibration is required for each water source. Testing for seasonal variation was not undertaken, but it may be assumed that the relationship is primarily temperature dependent and is not thought to be affected by any variations in organic matter. Further tests on a range of waters having differing chemical characteristics are required to confirm this test as a generic surrogate of disinfectant demand.

CONCLUSIONS
Two commonly used disinfectants, chlorine and chloramine, have been studied with the aim of developing a tool to

Table 5 | R² values for shorter demand time against longer demand times.

<table>
<thead>
<tr>
<th>Demand Time (d)</th>
<th>2-d Chlorine Demand</th>
<th>7-d Chlorine Demand</th>
<th>3-d Chloramine Demand</th>
<th>7-d Chloramine Demand</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-d</td>
<td>0.94</td>
<td>0.91</td>
<td>0.69</td>
<td>0.60</td>
</tr>
<tr>
<td>2-d</td>
<td>0.97</td>
<td>0.95</td>
<td>0.72</td>
<td>0.63</td>
</tr>
<tr>
<td>3-d</td>
<td>0.97</td>
<td>0.95</td>
<td>0.77</td>
<td>0.68</td>
</tr>
<tr>
<td>4-d</td>
<td>1.00</td>
<td>0.99</td>
<td>0.92</td>
<td>0.85</td>
</tr>
<tr>
<td>5-d</td>
<td>–</td>
<td>0.99</td>
<td>–</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Figure 4 | (a) Chlorine decay curves for Myponga South Australian water under different temperatures and an illustration of how to determine the chlorine residual equivalent. (b) Temperature calibration curves for chlorine and chloramine.
predict their demand. It is clear from this work that it would not be feasible to apply the same demand "sensor" to both disinfectants. From the study, three methods for the prediction of chlorine and two methods for the prediction of chloramine have been identified.

The chlorine demand predictions using surrogate parameters (DOC, UV254 and colour) and organic characterisation (the VHA fraction) have been based on a national database incorporating a large number of Australian water types and including seasonal variation. This therefore produces a chlorine prediction method which should be capable of being applied to any water in Australia at any time of the year. The use of the VHA fraction to predict chlorine demand is slightly more time consuming in that it cannot be measured online like UV254. However, it may be superior for certain waters to produce a more accurate demand prediction. The use of multiple surrogate parameters in combination is another possible alternative to the use of just a single parameter. However, accuracy is not improved beyond UV254 measurement as it also produced an $R^2$ value of 0.94 with the 3-d chlorine demand. From this study no surrogate parameter was identified which correlated well with chloramine demand over the range of water samples and seasonal variation. This probably explained why chloramine decay is strongly influenced by water chemistry (such as pH change) and the measured parameters selected in this work were not the main factors controlling chloramine decay. However, from this work, there does seem to be some link between the chloramine demand and the organic character (VHA) of the water. Further investigations may lead to the identification of a surrogate parameter for chloramine demand.

This study has also demonstrated that it is possible to determine the 3- and 7-d bulk water disinfection demand rapidly and accurately if the short term disinfectant demand (e.g. 3-h) is known. This method was found to work extremely well for chlorine demand. Rapid determination of chloramine demand (1-d) was also possible.

Finally, the elevated temperature method can be applied to both the chlorine and chloramine demand predictions. This method seems to be independent of water quality but requires an individual temperature calibration curve for each water source. Further investigations into this method could see the development of an automated system for use in the field.

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Development of tools for improved disinfection control


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APPENDIX III

The Benefits of On-line Water Quality Monitoring as a Component of Disinfection Management

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Rob Dexter, DCM Process Control Ltd
Dammika Vitanage, Sydney Water Corporation

INTRODUCTION

The goal of Water Quality Managers is to maintain a safe water supply that is palatable to customers. Maintaining a disinfectant residual throughout the distribution system is an effective way of ensuring the aesthetic and bacteriological quality of the water at the customer taps. Managing disinfection residual in distribution systems can be a very challenging task.

Chlorine is one of the most widely used disinfectants in drinking water treatment. The benefits of chlorine disinfection are well known and include low cost, a broad range of effectiveness and it has the added advantage of remaining active within the system for a considerable length of time. There are also a number of disadvantages in using free chlorine such as reaction with natural organic matter (NOM), formation of disinfection by-products (DBPs) etc, that make managing chlorine residuals within a distribution system difficult.

The use of alternative disinfection process such as chloramination, has proven to be beneficial in some situations, such as reduction in trihalomethane (THM) levels. Chloramination is the addition of ammonia and chlorine compounds separately into a pipe or tank (usually anhydrous ammonia and hypochlorous acid). Chloramination requires significantly more careful control of water chemistry than chlorination. Chlorine reacts with ammonia to form three inorganic chloramine species as shown in equations 1, 2, and 3. Monochloramine is the preferred disinfectant species, being more biocidal while having minimal taste and odour.

\[ \text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} \text{ (monochloramine)} + \text{H}_2\text{O} \] (1)
\[ \text{HOCl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 \text{ (dichloramine)} + \text{H}_2\text{O} \] (2)
\[ \text{HOCl} + \text{NHCl}_2 \rightarrow \text{NHCl}_3 \text{ (trichloramine)} + \text{H}_2\text{O} \] (3)

The formation of these competing reactions is highly dependent upon pH, the chlorine:ammonia ratio (Cl\(_2\):NH\(_3\) expressed as NH\(_3\)) and to a lesser extent temperature and contact time. Ideal conditions for monochloramine formation are those in which the pH range is between 8.0 to 8.5 with a Cl\(_2\):NH\(_3\) ratio of 4:1. By targeting these conditions, it is possible to ensure that monochloramine is the predominant species and so minimise the risk of water quality issues.

Chloramination was first successfully applied in 1926 in the US for taste and odour control, and became increasingly popular. Sydney’s water supplies were initially (1940) using chlorination as disinfection process and it was not until the early 1960s that the first trial of chloramination commenced. Currently, Sydney Water has 7 chloraminated and 6 chlorinated water systems. One main focus in chloraminated systems is to minimise nitrification and the practice adopted by Sydney Water is to optimise the total chlorine setpoint at the Water Filtration Plant and maintain a Cl\(_2\):NH\(_3\) ratio of 4:1 in the distribution system by locking up the free ammonia using secondary disinfection in the form of tablet dosing (calcium hypochlorite) at key reservoirs.

This paper describes a case study of monitoring water quality changes in the Woronora Distribution System in order to investigate the benefit of using an on-line water quality monitoring system as part of the disinfection management process.
EXPERIMENTAL

The S::CAN Spectro::lyer™ selected in this project comprises of a robust but sensitive submersible double beam full spectrum UV/Vis spectrometer with on-board data logging facility. It has no moving parts and has the advantage of reagent free operation which suits well for drinking water applications. It can provide direct readings of UV absorbance (abs) the same as the laboratory equipment and spectral data can be analysed using software to calculate several parameters (such as total organic carbon (TOC), dissolved organic carbon (DOC), nitrate, nitrite, turbidity, total suspended solids, particle size).

Table 1 Setup locations and duration of the two UV/Vis-spectrometers used in this study

<table>
<thead>
<tr>
<th>ID</th>
<th>Task Name</th>
<th>Start</th>
<th>Finish</th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
<th>Aug</th>
<th>Sep</th>
<th>Oct</th>
<th>Nov</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>WTP Inlet</td>
<td>Fri 2/09/05</td>
<td>Wed 28/09/05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>WTP Outlet</td>
<td>Wed 25/05/05</td>
<td>Wed 28/09/05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Menai Inlet</td>
<td>Tue 1/11/05</td>
<td>Mon 14/11/05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Menai Outlet</td>
<td>Fri 4/11/05</td>
<td>Mon 28/11/05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Bond Place</td>
<td>Mon 14/11/05</td>
<td>Mon 21/11/05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Bignell St</td>
<td>Mon 21/11/05</td>
<td>Mon 28/11/05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

During the study, two UV/Vis-spectrometers were used at some key locations to monitor changes in water quality. A smart monitoring program was setup to allow the use of only two units to study an entire arm of the distribution system (Table 1). The examples selected in this paper included 1) identifying water quality variation at the distribution system entry point, 2) impact of chloramine residual on organic character change along the distribution system, 3) water character change in main trunk and in further downstream the distribution network.

This investigation also included an extensive study of organic character change in several key sampling locations along the distribution system using an advanced organic characterisation techniques, high performance size exclusion chromatography (HPSEC), together with standard water quality parameters such as UVabs at 254 nm (UV_{254}), DOC etc. These techniques were applied to samples collected from

- Woronora source water (plant inlet)
- Woronora Water Filtration Plant (WFP) outlet
- Section Valve 3
- Menai reservoir inlet
- Menai reservoir outlet
- Illawong reservoir inlet
- Illawong reservoir outlet
- Customer taps close to the end of the network (Bond Place – Menai Zone and Bignell Street – Illawong Zone)

RESULTS AND DISCUSSION

Benefits of On-line Water Quality Monitoring

In recent years, considerable research effort has been expended to understand the impact of various forms of NOM on drinking water treatment processes. It is becoming a common practice for plant operators to perform regular UV_{254} measurement to assess treatment performance (van Leeuwen et al., 2005). UV/Vis absorbance measurement is a very simple but informative analytical technique, particularly when used in full spectrum mode (Langergraber et al., 2002).

The Woronora system consists of the catchment of the Woronora River (area 75 km²), which feeds into the Woronora Dam. The raw water quality is in the category of low colour, low turbidity and low DOC. The Woronora WFP has a production capacity of 160 ML/d and can be readily upgraded to 220 ML/d. The WFP incorporates a high rate contact filtration process employing ferric and polymers,
deep bed filters of coal and sand. It also includes a lime/CO₂ buffering process to control corrosion, and a manganese removal process (Veolia Water, 2006).

Figure 1 On-line monitoring of (a) UV₂₅₄ and (b) DOC for both raw and treated water over a period of time (1 month). The DOC data presented is only for illustration purpose.

One of the major benefits of using on-line monitoring instrument is the continuity of water quality information that can capture events usually missed by grab sample monitoring program. In Figure 1, the UV₂₅₄ and calculated DOC for both raw and treated water were presented. The DOC concentrations presented were not validated (no local calibration was performed at the time of monitoring) and may be different to the laboratory readings.

Figure 1 shows a conventional way of presenting on-line water quality data (parameter against time). It can be used to pickup water quality change events and the DOC calculating function can provide water quality managers a commonly used parameter to assess water quality. This demonstrated part of the benefits of using on-line instrumentation.

Identifying Water Quality Variation at the Distribution System Entry Point

One of the important aspects of using on-line water quality monitoring system is the ability to obtain real-time water quality data to allow operators a quick assessment / adjustment without delay (no need to wait for the laboratory analytical report). This will provide operators with a useful tool for maintaining stable water quality and it is believed to be a good practice to reduce the risk of having problems in the distribution system.

With the capability of recording a full spectrum continuously (ie, 5 min per spectrum or faster), more useful analytical information can be generated. However, this also prompted the need for a different way of presenting the information which is easily assessable and readable for operators. Several custom made softwares/procedures were introduced to process and visualise the spectral change over time. Although during an event the absorbance signal may vary and can be picked up by conventional single wavelength signal against time plot, however, the use of derivative spectrum (a different mode of presenting the spectral information) is easier to distinguish changes. This is particularly useful for application where hundreds of spectra are required to be inspected visually. The software included a fast screening step to display the derivative spectra to identify a period of interest then “zoom in” for further investigation which can include more detailed spectral analyses, such as 3-D, contour or colour map plot to identify relative changes in spectra against time and together with other available on-line water quality or operational data to identify the cause of event and determine possible corrective actions.

Below is an example of identifying the cause of water quality change at the WFP by monitoring the treated water quality (WFP outlet). During the monitoring period a very small spike (reduction of UVabs signal / calculated DOC) was observed, this probably was not notifiable with normal operational monitoring. By inspecting the derivative spectra as described previously, a spectral shift was clearly identified (Figure 2). The derivative spectrum at the spike occurred was a standout from the others, with the additional on-line data, it was noted that the WFP water flow was reduced during that period. The reduction of UV₂₅₄ signal generally refers to the reduction of DOC / chlorine demand.
and the chlorine dosing system would automatically adjust the dose via a feedback control loop based on chlorine residual at the outlet.

**Figure 2** Illustration of the advantage of using UV/Vis-spectrometer for feed-forward control of the chlorine dosing system at the WFP.

From the chlorine dosing record, the chlorine dose was also automatically reduced, however, this also showed the chlorine demand prediction algorithm detected the change 20 min ahead compared with the conventional feedback control. This also demonstrated that the potential application of using the UV/Vis-spectrometer signal for feed-forward control of the chlorine dosing system. The response of the control can be improved over the current feedback control based on the chlorine residual at the storage tank.

**Impact of Chloramine Residual on Organic Character Change along the Distribution System**

Organic matter is one of the key water parameters related to disinfection and distribution system management. UV absorbance measurement is a good tool to monitor organics in water and in some cases both the concentration and character are important. One of the aims of this project is to monitor organic character change along the distribution system in order to identify issues and develop management strategy based on water quality change. The difficulty of using UV absorbance for distribution system investigation is the chloramine residual in the water as chloramine contributes to UV absorbance signal (Figure 3).
In this part of the investigation, an advanced organic characterisation tool was used in conjunction with on-line UV absorbance measurement. HPSEC is a laboratory based analytical technique. It is a simple characterisation technique for NOM. It separates NOM constituents based on a differential permeation process, according to molecular weight (size). It is well understood that chlorination can alter organic character. This was demonstrated by the change of molecular weight distribution profile (chromatogram) after chlorination and chloramination above 5 mg/L as total chlorine (Chow et al., 2006). In Figure 4, the molecular weight profiles (500 to 2000 Da) from samples collected at key locations along the Woronora distribution system were very similar (almost identical). These results confirmed that chloramine concentrations below 2 mg/L as total chlorine have no impact on organic character (molecular weight profile).

Also in this study, we have discovered extra analytical information can be obtained from HPSEC to study chloraminated distribution systems. There were several low molecular weight peaks present in the chromatogram which were believed to be related to chloramine rather than organic compounds. It also appeared that the size of these peaks lines well with detention of the distribution system (larger peak in downstream location). Further investigation is underway.
By comparing the samples collected at different sampling locations, these "chloramine" peaks showed large daily variation in sampling locations with nitrification history. This may provide some useful information in disinfection management. More importantly, this finding also demonstrated that the commonly used UV$_{254}$ will not be suitable to monitor organics in chloraminated system, as the change in the UV absorbance signal may also be due to the change in chloramine concentration. In Figure 5, the plot of total chlorine against time indicated total chlorine increased after tablet dosing and the same trend was registered by the UV$_{254}$ measurement. This result confirmed chloramine residual can impact UV$_{254}$ measurement. This observation can also be considered as an additional application of using UV$_{254}$ to monitor chloramine residuals.

During November 2005 a total of 22 samples from Menai tank outlet were analysed for molecular weight distribution using HPSEC. The molecular weight profile of the "organic" region (500 to 2000 Da) was almost identical, except there was observed variation in the low molecular weight region (Figure 6). This confirmed that part of the variation in 254nm was caused by chloramine residual rather than organics. A new parameter "compensated 254nm" based on using 265nm (chloramine shows a strongest signal in 265nm) was developed to estimate the contribution of the "chloramine" component in UV$_{254}$ (organic) measurement.

Figure 5 On-line data of UV$_{254}$ and total chlorine at the Menai outlet. ♦ Marked the time for chlorine tablet dosing and the UV/Vis-spectrometer signal between 18/11/05 to 24/11/05 was removed due to unknown problem.

Figure 6 The molecular weight profile of a series of samples collected from the Menai outlet between 2/11/05 to 28/11/05. Only five samples were shown.
Water character change in main trunk and in further downstream the distribution network.
Water quality change between two locations can be used to assess the conditions of a tank, section of a pipe, or problematic zone. This information can be used for an early warning system and setup corrective action plans. Two UV/Vis-spectrometers were installed at two locations, upstream and downstream of the specific area of interest. The assessment was based on the signal different between the two on-line units. The assessment procedure was similar as previously mentioned. In addition, due to the requirement of comparing signals from two units, specific software was developed for averaging and substraction.

Several studies had been conducted in the Menai zone. One of the UV/Vis-spectrometers was installed at the Menai tank outlet over one month period and the second unit was located first at the Menai tank inlet, Bond Place (which is a customer tap located close to the Menai tank) and Bignell Street (a customer tap located in the Illawong zone – close to the end of the distribution system). Based on this setup, the Menai tank, section from Menai outlet to Bond Place and Menai outlet to Bignell Street can be assessed. However, this part of the result will not be shown in this manuscript as the result is best shown in computer animation mode.

CONCLUSIONS
Water Quality Managers throughout the world recognise the value in maintaining disinfectant residual throughout the distribution system in order to maintain water quality at the customer tap. This often presents a significant challenge for water operators and it is a continuous effort to develop better tools for this demanding task. This paper presents some examples of using on-line water quality monitoring with the combination of using data processing software as a tool to assist water operators to maintain stable water quality. Although this work did not demonstrate the real-time control of chlorine dosing at the WFP, this has certainly illustrated the feasibility of using on-line UV absorbance measurement for feed-forward control in the first example. The second example demonstrated tablet dosing (variation of chloramine concentration) at the Menai tank can impact on UV<sub>254</sub> measurement for organic character study. However, with the processing power of the software, the UVabs signal contributed by chloramine can be compensated. Due to the low chloramine concentration used in the Woronora system, organic character change along the distribution system was not observed. Thus, we did not demonstrate the usefulness of the compensated UV<sub>254</sub> (organic) measurement in this study. This part should be repeated in a distribution system which operates at higher chloramine concentration. This paper only reported a section of potential applications using on-line monitoring tools in treatment and distribution system management but highlighted the need to understand the spectral response to the water structure itself rather than relying on a single frequency as a surrogate. This extra spectral information can be used as a tool to achieve the goal of water quality improvement. A new CRC Water Quality and Treatment project has started mid this year to evaluate the benefits of using on-line water quality monitoring tools for the drinking water industry.

ACKNOWLEDGMENT
The authors wish to thank Luke Sutherland-Stacey (DCM Process Control), Colin Storey (Veolia Water), Phil Duker (Sydney Water), Philipp Kuntke and Leon Li (AWQC) for their contribution of this work.

REFERENCES
APPENDIX IV

Water Quality Data
Cardinia (VIC)
Colour Seasonal Variation

Turbidity Seasonal Variation
Cardinia (VIC)
TOC and DOC Seasonal Variation

UV absorbance Seasonal Variation
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

Cardinia (VIC)
SUVA (UV_{254}/DOC) Seasonal Variation

SUVA (m^{-1}mg^{-1}L)
Specific Colour (Colour/DOC) Seasonal Variation
Cardinia (VIC)
High Performance Size Exclusion Chromatography (HPSEC) Seasonal Variation
Raw Water
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

Cardinia (VIC)
Rapid Fractionation Seasonal Variation (Raw Water)
Darwin River (NT)
Colour Seasonal Variation

Turbidity Seasonal Variation
Darwin River (NT)
TOC and DOC Seasonal Variation

UV absorbance Seasonal Variation
Darwin River (NT)
SUVA ($\text{UV}_{254}$/DOC) Seasonal Variation

SUVA ($\text{m}^{-1}\text{mg}^{-1}\text{L}$)
Specific Colour (Colour/DOC) Seasonal Variation
Darwin River (NT)
High Performance Size Exclusion Chromatography (HPSEC) Seasonal Variation
Raw Water
Darwin River (NT)
Rapid Fractionation Seasonal Variation (Raw Water)

DOC (mg/L)

% DOC (%)
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

Hinze Dam, Gold Coast (QLD)
Colour Seasonal Variation

![Colour Seasonal Variation Chart]

Turbidity Seasonal Variation

![Turbidity Seasonal Variation Chart]
Hinze Dam, Gold Coast (QLD)
TOC and DOC Seasonal Variation

UV absorbance Seasonal Variation
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

Hinze Dam, Gold Coast (QLD)
SUVA (UV<sub>254</sub>/DOC) Seasonal Variation

SUVA (m<sup>-1</sup>mg<sup>-1</sup>L)
Specific Colour (Colour/DOC) Seasonal Variation

SUVA (m<sup>-1</sup>mg<sup>-1</sup>L)
Specific Colour (Colour/DOC) Seasonal Variation

Raw
Treated
Hinze Dam, Gold Coast (QLD)
High Performance Size Exclusion Chromatography (HPSEC) Seasonal Variation
Raw Water

Apparent Molecular Weight (Da)

Treated Water

Apparent Molecular Weight (Da)
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

Hinze Dam, Gold Coast (QLD)
Rapid Fractionation Seasonal Variation (Raw Water)
Hinze Dam, Gold Coast (QLD)
Rapid Fractionation Seasonal Variation (Treated Water)
Happy Valley (SA)
Colour Seasonal Variation

![Graph showing Colour Seasonal Variation]

Turbidity Seasonal Variation

![Graph showing Turbidity Seasonal Variation]
Happy Valley (SA)
TOC and DOC Seasonal Variation

OC (mg/L)

Jun-03  Sep-03  Dec-03  Mar-04  Jun-04  Sep-04  Dec-04  Mar-05

UV absorbance Seasonal Variation

UV$_{254}$ (cm$^{-1}$)

Jun-03  Sep-03  Dec-03  Mar-04  Jun-04  Sep-04  Dec-04  Mar-05
Happy Valley (SA)
SUVA (UV$_{254}$/DOC) Seasonal Variation

SUVA (m$^{-1}$mg$^{-1}$L)
Specific Colour (Colour/DOC) Seasonal Variation
Happy Valley (SA)
High Performance Size Exclusion Chromatography (HPSEC) Seasonal Variation
Raw Water

Apparent Molecular Weight (Da)

Treated Water

Apparent Molecular Weight (Da)
Happy Valley (SA)
Rapid Fractionation Seasonal Variation (Raw Water)
Happy Valley (SA)
Rapid Fractionation Seasonal Variation (Treated Water)

**DOC (mg/L)**

- VHA
- SHA
- CHA
- NEU
- Total DOC

**% DOC (%)**

- VHA
- SHA
- CHA
- NEU

<table>
<thead>
<tr>
<th>Month</th>
<th>DOC (mg/L)</th>
<th>% DOC (%)</th>
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<tbody>
<tr>
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<td>Dec-04</td>
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<tr>
<td>Mar-05</td>
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</table>
Jandakot (WA)
Colour Seasonal Variation

Turbidity Seasonal Variation
Jandakot (WA)
TOC and DOC Seasonal Variation

UV absorbance Seasonal Variation
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

Jandakot (WA)
SUVA (UV$_{254}$/DOC) Seasonal Variation

SUVA (m$^{-3}$mg$^{-1}$L)
Specific Colour (Colour/DOC) Seasonal Variation

Sp Col (HU/mg)
Jandakot (WA)
High Performance Size Exclusion Chromatography (HPSEC) Seasonal Variation
Raw Water

Apparent Molecular Weight (Da)

Treated Water

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Jandakot (WA)
Rapid Fractionation Seasonal Variation (Raw Water)

DOC (mg/L)

% DOC (%)

VHA
SHA
CHA
NEU
Total DOC

Jun-03 Sep-03 Dec-03 Mar-04 Jun-04 Sep-04 Dec-04 Mar-05
Jandakot (WA)
Rapid Fractionation Seasonal Variation (Treated Water)
Moondara (VIC)
Colour Seasonal Variation

Turbidity Seasonal Variation
Moondara (VIC)
TOC and DOC Seasonal Variation

UV absorbance Seasonal Variation
Moondara (VIC)
SUVA (UV<sub>254</sub>/DOC) Seasonal Variation

SUVA (m<sup>-1</sup>mg<sup>-1</sup>L)
Specific Colour (Colour/DOC) Seasonal Variation

- Raw
- Treated
Moondara (VIC)
High Performance Size Exclusion Chromatography (HPSEC) Seasonal Variation
Raw Water

Apparent Molecular Weight (Da)

Treated Water

Apparent Molecular Weight (Da)
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

Moondara (VIC)
Rapid Fractionation Seasonal Variation (Raw Water)
Moondara (VIC)
Rapid Fractionation Seasonal Variation (Treated Water)
Morgan (SA)

Colour Seasonal Variation

Turbidity Seasonal Variation
Morgan (SA)
TOC and DOC Seasonal Variation

UV absorbance Seasonal Variation
Morgan (SA)
SUVA (UV$_{254}$/DOC) Seasonal Variation

SUVA (m$^{-1}$mg$^{-1}$L)
Specific Colour (Colour/DOC) Seasonal Variation
Morgan (SA)
High Performance Size Exclusion Chromatography (HPSEC) Seasonal Variation
Raw Water

Apparent Molecular Weight (Da)

Treated Water

Abs@260nm

0.000
0.005
0.010
0.015
0.020
0.025
0.030

100
1000
10000
100000
1000000

Jun-03
Sep-03
Dec-03
Mar-04
Jun-04
Sep-04
Dec-04
Mar-05
Morgan (SA)
Rapid Fractionation Seasonal Variation (Raw Water)
Morgan (SA)
Rapid Fractionation Seasonal Variation (Treated Water)

![Graph showing DOC (mg/L) and % DOC (%) over time from Jun-03 to Mar-05.]

- DOC (mg/L) graph:
  - VHA
  - SHA
  - CHA
  - NEU
  - Total DOC

- % DOC (%) graph:
  - VHA
  - SHA
  - CHA
  - NEU
Myponga (SA)
Colour Seasonal Variation

Turbidity Seasonal Variation
Myponga (SA)
TOC and DOC Seasonal Variation

UV absorbance Seasonal Variation
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

Myponga (SA)
SUVA (UV$_{254}$/DOC) Seasonal Variation

SUVA (m$^{-1}$mg$^{-1}$L)
Specific Colour (Colour/DOC) Seasonal Variation

SUVA (m$^{-1}$mg$^{-1}$L)
Specific Colour (Colour/DOC) Seasonal Variation
Myponga (SA)
High Performance Size Exclusion Chromatography (HPSEC) Seasonal Variation
Raw Water

Apparent Molecular Weight (Da)

Treated Water

Apparent Molecular Weight (Da)
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

Myponga (SA)
Rapid Fractionation Seasonal Variation (Raw Water)

[Graph showing DOC (mg/L) and % DOC (%) for different months from June 2003 to March 2005, with four categories: VHA, SHA, CHA, and NEU, and the Total DOC.]

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Myponga (SA)
Rapid Fractionation Seasonal Variation (Treated Water)

DOC (mg/L)

% DOC (%)
Woronora (NSW)
Colour Seasonal Variation

Turbidity Seasonal Variation
Woronora (NSW)
TOC and DOC Seasonal Variation

UV absorbance Seasonal Variation
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL

Woronora (NSW)
SUVA (UV\textsubscript{254}/DOC) Seasonal Variation

SUVA (m\textsuperscript{-1}mg\textsuperscript{-1}L)

Specific Colour (Colour/DOC) Seasonal Variation

SUVA (m\textsuperscript{-1}mg\textsuperscript{-1}L)
Woronora (NSW)
High Performance Size Exclusion Chromatography (HPSEC) Seasonal Variation
Raw Water

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<th>Dec-03</th>
<th>Mar-04</th>
<th>Jun-04</th>
<th>Sep-04</th>
<th>Dec-04</th>
<th>Mar-05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abs@260nm</td>
<td>0.015</td>
<td>0.012</td>
<td>0.009</td>
<td>0.006</td>
<td>0.003</td>
<td>0.003</td>
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<tr>
<td>Apparent Molecular Weight (Da)</td>
<td></td>
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<td></td>
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</table>

Treated Water

<table>
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<tr>
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<th>Dec-03</th>
<th>Mar-04</th>
<th>Jun-04</th>
<th>Sep-04</th>
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<tr>
<td>Apparent Molecular Weight (Da)</td>
<td></td>
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</tr>
</tbody>
</table>
Woronora (NSW)
Rapid Fractionation Seasonal Variation (Raw Water)
Woronora (NSW)
Rapid Fractionation Seasonal Variation (Treated Water)

Fiona Fitzgerald, Joachim Buff, Mike Holmes, Dr. Alexander Badalyan

United Water International Pty Ltd, Adelaide, University of South Australia, Adelaide, Australian Water Quality Centre, Adelaide
FOREWORD

This is report number 3 of a series of reports that have been produced in the CRC Water Quality and Treatment Project 2.5.0.1 Development of Tools for the Improved Control of Disinfectant Residual in Distribution Systems.

Report number one is intended to provide persons interested in the design, operation and water quality aspects of water distribution system with an introduction to the project. It describes the aims of the project and provides an overview of the various work packages included in it.

Report number two covers development and application of rapid sensors to determine bulk water chlorine and chloramine demand. It is useful to persons interested in water quality and chlorination/chloramination process control.

Report number three describes the methodology used and results obtained from a laboratory based evaluation to study to assess the performance of a number of commercially available online disinfectant residual analysers. It is useful to persons interested in measuring disinfectant residual online as well as evaluating and selecting online disinfectant residual analysers.

Report number four is a PhD thesis describing the development and evaluation of a prototype software suite to optimise chemical disinfection control in two full scale distribution systems used as case studies to the project. The software includes an artificial neural network module. The study aims to develop control algorithms that can be used to predict disinfectant residual and chemical dosing requirements. The thesis will be of most value to persons interested in developing knowledge about ANNs.
EXECUTIVE SUMMARY

Background
This study has been completed as part the CRC Water Quality and Treatment project 2.5.0.1. - “Development of Tools for Improved Disinfection Residual in Distribution Systems”. Discussions with CRC WQ&T industry partners who represent a large number of water utilities in Australia identified an urgent need for cost-effective online disinfectant residual analysers that can be installed in water distribution systems (WDS). The Australian Drinking water guidelines (ADWG, 2004) recognise chlorination as a critical control point and make reference to continuous online monitoring of chlorine residual in WDS applications. A key aim of project 2.5.0.1. is to apply data obtained from online monitors located in WTP and WDS location to artificial neural network models (ANN’s) to improve the control of disinfectant residual (Holmes et al 2005). For these reasons, it is important to identify cost effective reliable online disinfection analysers that can be used in WDS applications.

The ideal online disinfectant residual analyser would perform accurately and reliably for several weeks or months unattended without the need for calibration or reagent replacement, have low capital cost, and have low maintenance requirements. The analyser should have the ability to be integrated into a security control and data acquisition (SCADA) to provide early warning of water quality deterioration failure or for process control needs.

Nine free chlorine analysers, five total chlorine/monochloramine analysers and three ammonia (free and total ammonia) analysers were loaned by instrument suppliers and rigorously evaluated under laboratory conditions (ISO 1990, ISO 2003). None of these analysers were specifically designed for use in a WDS application (Table ES1). A test rig was used to recirculate a common feed water stream to individual analyser. Output from the analysers was recorded using a data logger. Free chlorine, total chlorine and monochloramine residual were confirmed using a titration method (APHA, 1998). Ammonia residual was confirmed using a commercial test kit (Hach DR 890, Hach Company, Loveland Co, USA).

Results and discussion
Analysers can be identified as indicated in Table 3.1. Summarised results for free chlorine, total chlorine/monochloramine, and free and total ammonia online analysers are presented in Tables 3.2-3.4, respectively. A brief explanation of the online analyser key performance indicators (KPI) used in this report is provided (ISO 1990, ISO 2003).

Response time, delay time and rise time characterise an analyser’s response to changing sample concentration over a short time period. The lower the value found for these indicators, the faster the analyser will respond to concentration changes. The response time is defined as the “time interval between the instant when the on-line sensor/analyser equipment is subjected to an abrupt change in determinant value and the instant when the readings cross the limits of (and remain inside) a band defined by 90% and 110% of the difference between the initial and final value of abrupt change”. The delay time is defined as the “time interval between the instant when the on-line sensor/equipment is subjected to an abrupt change in determinant value and the instant when the readings pass (and remain beyond) 10% of the difference between the initial and final value of the abrupt change”. The rise time is defined as the “difference between response time and the delay time when the abrupt change in determinant value is positive”. Similarly, the fall time is defined as the “difference between response time and the delay time when the abrupt change in determinant value is negative”.

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Table 3.1 Analyser codes for Tables 3.2-3.4.

<table>
<thead>
<tr>
<th>Code</th>
<th>Free Chlorine</th>
<th>Total Chlorine /Monochloramine</th>
<th>Free and Total Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Prominent – Dulcotest Sensor Type CLE</td>
<td>Analytical Technology, Inc. – ATI Model A 15/63</td>
<td>Applikon - ADI 2018</td>
</tr>
<tr>
<td>2</td>
<td>Prominent – Dulcometer D1C</td>
<td>Prominent – Dulcometer 1</td>
<td>Endress &amp; Hauser – StamoLys CA 71 AM</td>
</tr>
<tr>
<td>3</td>
<td>ATI Model A 15/62</td>
<td>Wallace &amp; Tieman – Depolox 3 plus</td>
<td>Systea – MicroMac – Ammonia</td>
</tr>
<tr>
<td>4</td>
<td>Endress &amp; Houser CCS141</td>
<td></td>
<td>Applikon – Alert 2004</td>
</tr>
<tr>
<td>5</td>
<td>B &amp; C Electronics CL 7685</td>
<td>Systea – MicroMac – Total Chlorine</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Yokogawa Model FC400G-63*A/Z</td>
<td>Systea – MicroMac – Monochloramine</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Hach CL17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Wallace &amp; Tieman - Depolox 3 plus (membrane style)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Wallace &amp; Tieman – Depolox 3 plus (bare electrode style)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Linearity is the “condition in which measurements made on calibration solutions having determinant values spanning the stated range of the on-line sensor/analysing equipment have a straight line relationship with the calibration solution determinant values”. This is expressed as an $R^2$ value and the closer the $R^2$ value is to 1, the better the linearity performance. The coefficient of variation (COV) is defined as the “ratio of the standard deviation of the on-line sensor/analysing equipment to the mean of the working range of the equipment”. The lower the COV, the closer the results obtained from an analyser to the reference concentration. The limit of detection (LOD) is measured using a 5% test solution and is the “lowest value, significantly greater than zero, of a determinant that can be detected”. The smaller the LOD, the smaller the disinfectant concentration that an analyser can detect. The limit of quantification (LOQ) is also measured using a 5% test solution and is the “lowest value of determinant that can be determined with an acceptable level of accuracy and precision”. The LOD is usually a larger value than the LOQ. Lowest detectable change (LDC) is measured using a 20 to 80% test solution range and is the “smallest significantly measurable difference between two measurements”. The lower the value of LOD, LOQ and LDC, the better the performance of an analyser.

Repeatability and day-to-day repeatability are defined as “precision under repeatability and precision under day-to-day repeatability conditions”. Bias is the “consistent deviation of the measured value from an accepted reference value” and this value should be subtracted from the measured analyser result. Short-term drift (ShTD) is the “slope of the regression line derived from a series of measurements carried out on the same calibration solution during laboratory testing, and expressed as a percentage of the measurement range over a 24 hour period”. The memory effect is a “temporary or permanent dependence of readings on one or several previous values of the determinant”. The lower, the bias, repeatability, short term drift and memory, the better the performance of an analyser.

Interference can give rise to “undesired output signal caused by a property(ies)/substance(s) other than the one being measured”. The lower the dependence (%) upon a parameter, the better the performance of an analyser when subject to changes in concentration of that parameter.
Table 3.2 Summary of KPI's for free chlorine analysers.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<th>6</th>
<th>7</th>
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<th>9</th>
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</thead>
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<td>+ve/-ve Response Time</td>
<td>s</td>
<td>81.2</td>
<td>202.2</td>
<td>55.2</td>
<td>109.7</td>
<td>82.3</td>
<td>59.9</td>
<td>128.8</td>
<td>89.6</td>
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<td>91.6</td>
<td>145.8</td>
<td>75.6</td>
<td>84.0</td>
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<td>100.0</td>
<td>47.2</td>
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<tr>
<td>Linearity - equation</td>
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<td>0.795x</td>
<td>1.066x</td>
<td>1.047x</td>
<td>1.045x</td>
<td>0.985x</td>
<td>1.045x</td>
<td>1.024x</td>
<td>0.626x</td>
<td>0.689x</td>
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<td>Linearity – R²</td>
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<td>0.9716</td>
<td>0.8829</td>
<td>0.8971</td>
<td>0.7967</td>
<td>0.9599</td>
<td>0.9554</td>
<td>0.6425</td>
<td>0.6794</td>
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<tr>
<td>COV</td>
<td>mg/L</td>
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<td>0.16</td>
<td>0.27</td>
<td>0.22</td>
<td>0.27</td>
<td>0.14</td>
<td>0.15</td>
<td>0.61</td>
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<td>mg/L</td>
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<td>0.10</td>
<td>0.07</td>
<td>0.10</td>
<td>0.06</td>
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<td>0.03</td>
<td>0.02</td>
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<td>LOQ</td>
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<td>0.32</td>
<td>0.22</td>
<td>0.32</td>
<td>0.22</td>
<td>0.19</td>
<td>0.10</td>
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<td>Repeatability, 20% test solution</td>
<td>mg/L</td>
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<td>0.01</td>
<td>0.05</td>
<td>0.04</td>
<td>0.06</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Repeatability, 80% test solution</td>
<td>mg/L</td>
<td>0.03</td>
<td>0.08</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
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<td>0.02</td>
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<tr>
<td>Day-to-day repeatability, 35%</td>
<td>mg/L</td>
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<td>0.06</td>
<td>0.20</td>
<td>0.06</td>
<td>0.12</td>
<td>0.21</td>
<td>0.07</td>
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<td>test solution</td>
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<tr>
<td>Day-to-day</td>
<td>mg/L</td>
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<td>repeatability, 65% test solution</td>
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<tr>
<td>LDC, 20% test solution</td>
<td>mg/L</td>
<td>0.15</td>
<td>0.04</td>
<td>0.14</td>
<td>0.12</td>
<td>0.19</td>
<td>0.08</td>
<td>0.06</td>
<td>0.06</td>
<td>0.08</td>
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<tr>
<td>LDC, 80% test solution</td>
<td>mg/L</td>
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<td>0.23</td>
<td>0.10</td>
<td>0.06</td>
<td>0.08</td>
<td>0.02</td>
<td>0.13</td>
<td>0.02</td>
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<td>Short-term drift</td>
<td>%</td>
<td>0.55</td>
<td>0.00</td>
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<td>1.22</td>
<td>1.39</td>
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<td>1.81</td>
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<td>0.04-No</td>
<td>0.00-No</td>
<td>0.16-Yes</td>
<td>0.04-No</td>
<td>0.06-No</td>
<td>0.05-No</td>
<td>0.06-No</td>
<td>-0.05-No</td>
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</tr>
<tr>
<td>Conductivity dependence</td>
<td>%</td>
<td>1.5</td>
<td>2.7</td>
<td>3.0</td>
<td>2.3</td>
<td>2.5</td>
<td>14.1</td>
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</table>
### Table 3.3 Summary of KPI's for total chlorine/monochloramine analysers.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Monitors</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Measuring technique</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measuring technique</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals required</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemicals required</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ve/-ve Response Time</td>
<td>s</td>
<td>361/155</td>
</tr>
<tr>
<td>Linearity, eq.</td>
<td></td>
<td>0.8549x</td>
</tr>
<tr>
<td>Linearity – R^2</td>
<td></td>
<td>0.9335</td>
</tr>
<tr>
<td>COV</td>
<td>mg/L</td>
<td>28</td>
</tr>
<tr>
<td>LOD</td>
<td>mg/L</td>
<td>0.023</td>
</tr>
<tr>
<td>LOQ</td>
<td>mg/L</td>
<td>0.077</td>
</tr>
<tr>
<td>Repeatability for 20% test solution</td>
<td>mg/L</td>
<td>0.03</td>
</tr>
<tr>
<td>Repeatability for 80% test solution</td>
<td>mg/L</td>
<td>0.09</td>
</tr>
<tr>
<td>35% test solution day-to-day</td>
<td>mg/L</td>
<td>0.11</td>
</tr>
<tr>
<td>Repeatability</td>
<td></td>
<td></td>
</tr>
<tr>
<td>65% test solution day-to-day</td>
<td>mg/L</td>
<td>0.34</td>
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<td></td>
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<tr>
<td>LSC for 20% test solution</td>
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<td>0.09</td>
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<tr>
<td>LSC for 80% test solution</td>
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<td>0.26</td>
</tr>
<tr>
<td>Short-term drift</td>
<td>%</td>
<td>7.77</td>
</tr>
<tr>
<td>Memory effect</td>
<td>mg/L</td>
<td>0.02-No</td>
</tr>
<tr>
<td>pH dependence</td>
<td>%</td>
<td>44</td>
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<tr>
<td>Conductivity dependence</td>
<td>%</td>
<td>0.90</td>
</tr>
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<td>Parameter</td>
<td>Units</td>
<td>Analyser 1</td>
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<td>--------------------------------------------------</td>
<td>-------</td>
<td>------------</td>
</tr>
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<td>Measuring technique</td>
<td></td>
<td>Ammonia Selective Electrode</td>
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<td>Chemical Disposal</td>
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</tr>
<tr>
<td>+ve/-ve Response Time</td>
<td>s</td>
<td>1370/1452</td>
</tr>
<tr>
<td>Linearity – equation</td>
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<td>1.3297x</td>
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<tr>
<td>Linearity – $R^2$</td>
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<td>0.9962</td>
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<tr>
<td>COV</td>
<td>mg/L</td>
<td>34.20</td>
</tr>
<tr>
<td>LOD</td>
<td>mg/L</td>
<td>0.016</td>
</tr>
<tr>
<td>LOQ</td>
<td>mg/L</td>
<td>0.052</td>
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<tr>
<td>Repeatability for 20% test solution</td>
<td>mg/L</td>
<td>0.02</td>
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<tr>
<td>Repeatability for 80% test solution</td>
<td>mg/L</td>
<td>0.02</td>
</tr>
<tr>
<td>Day-to-day repeatability for 35% test solution</td>
<td>mg/L</td>
<td>0.05</td>
</tr>
<tr>
<td>Day-to-day repeatability for 65% test solution</td>
<td>mg/L</td>
<td>0.10</td>
</tr>
<tr>
<td>Lowest detectable change (LDC) for 20% test solution</td>
<td>mg/L</td>
<td>0.054</td>
</tr>
<tr>
<td>Lowest detectable change (LDC) for 80% test solution</td>
<td>mg/L</td>
<td>0.063</td>
</tr>
<tr>
<td>Short-term Drift</td>
<td>%</td>
<td>2.29</td>
</tr>
<tr>
<td>Memory effect</td>
<td>mg/L</td>
<td>0.07-Yes</td>
</tr>
<tr>
<td>pH dependence</td>
<td>%</td>
<td>3.7</td>
</tr>
<tr>
<td>Conductivity dependence</td>
<td>%</td>
<td>2.0</td>
</tr>
</tbody>
</table>
1 INTRODUCTION

1.1 Why do this research?

The biggest risk to public health when managing the supply of potable water arises from microbiologically contaminated water (NHMRC/NRMMC, 2004). Primary disinfection is achieved in many water treatment plants (WTPs) by the addition of chlorine (gaseous or liquid hypochlorite) to ensure the destruction of organisms potentially infectious to humans. Effective management of water quality in the water distribution system (WDS) is vital in delivering good quality water to customs and the application of online analysers can play an important role in achieving this.

This work has been undertaken as part of the CRC Water Quality and Treatment (WQ&T) research project 2.5.0.1., Development of Tools for Improved Disinfection Control within Water Distribution System. A key aim of the project is to apply online data obtained from WTP and WDS location to artificial neural network models (ANN's) to improve the control of disinfection residual in the WDS (Holmes et al 2005).

1.2 Background

1.2.1 What to measure?

Disinfectant residual water quality parameters that are commonly measured in WDS applications include free chlorine, total chlorine, monochloramine, free ammonia and total ammonia. A brief discussion of these measured parameters is presented:

- Free chlorine is the sum of the concentration of hypochlorite ion (OCl\(^-\)) and hypochlorous acid (HOCl). The distribution between these species depends on pH value and temperature of water, and to a lesser extent, on conductivity.
- Total chlorine is the sum of free and combined chlorine, the latter representing the residual chlorine combined with ammonia (chloramines) or organic amines in water.
- Monochloramine (NH\(_2\)Cl) is the preferred disinfectant used during chloramination.
- Free ammonia is the sum of the concentration of ammonium ion, NH\(_4^+\), (or ionised ammonia) and ammonia, NH\(_3\), (or unionised ammonia), which are represented in water in equilibrium. Their proportion depends on water temperature and pH.
- Total ammonia is the sum of the concentration of free ammonia plus ammonia that combines with chlorine to form chloramines.

1.2.2 Requirements for WDS online analysers

The ideal online disinfectant residual analyser would have low capital cost, low maintenance requirements and perform accurately and reliably for several weeks or months unattended without the need for calibration or reagent replacement.

1.3 What is in this report, and who should read it?

This report describes the methodology used for the evaluation of a number of commercially available disinfectant residual analysers. It describes and explains the key performance indicators (KPI) which are used for the evaluation of the performance of an analyser. The report gives detailed and summarised results, and provides performance criteria for individual residual analysers. The report concludes with some guidance when selecting an online disinfectant residual analyser for an application.

Anyone looking to specify an online disinfectant residual analyser should read this report. The approach taken in this study can also be applied to any online water quality analyser, and this report will be of use to anyone wishing to understand online analyser performance characteristics. It explains what performance characteristics are available, how they are determined and calculated, and how the experimentally obtained results may be interpreted. This knowledge can be used to improve the selection of an online water quality analyser.
Techniques for online measurement of disinfectant residual, description of on-line analysers evaluated, experimental methods for analysers’ evaluation and online key performance indicators description are discussed in detail in chapters 6.1 – 6.4 in the Appendices.

Chapter 6.1 gives a detailed description of various analytical methods that can be used to measure free and total chlorine, monochloramine as well free and total ammonia in water. They include colorimetric, polarographic membrane electrode, amperometric electrodes, phenate and ion selective electrode methods.

Detailed description, technical data, operational performance, and images of all online residual disinfectant analysers are presented in chapter 6.2, and should be used for assistance in the evaluation of analyser’s operational performance against key performance parameters.

Chapter 6.3 scribes: the analytical methods for the measurement of disinfectant residual concentration in water samples; a description of the test rig and protocol used to evaluate the online analysers; and the data logging facility.

Twelve KPIs defined in ISO Standard 15839 (2003) are described in detail in chapter 6.4 providing the reader with a better understanding of their meaning and how their values can be used for the analyser performance evaluation, simple numerical examples are given in this chapter.

**IMPORTANT.** This report does not compare disinfectant residual analysers, nor does it recommend any particular analyser. This can only be done by individual water utility in the light of their business needs.
1.4 Aims and objectives

A key aim of the CRC WQ&T project 2.5.0.1 is to evaluate commercially available online disinfectant residual analysers that can be used in WDS and remote location applications.

This aim of this study is to undertake a thorough evaluation of several free chlorine, total chlorine, monochloramine and ammonia online monitors. Analysers were tested in the laboratory environment using methodology based on ISO standards (ISO 15839, 2003 and ISO 8466-1 1990). During these trials, the recommendations of a Testing Report (ITA 1990) were taken into account during test rig assembly and data processing.

The objective of this report is to provide an explanation of KPI used in this study together with KPI data obtained from laboratory trials. This information can be used by a prospective user when selecting an analyser.
2 ONLINE ANALYSER EVALUATION METHODOLOGY

2.1 Literature review
A literature review of available methods for the assessment of online analysers was undertaken and two key reports were identified:

- ISO Standard 15839 (ISO 2003), Water Quality–On-line sensor/analysing equipment for water – Specifications and performance tests; and

The methodology used in this evaluation study was based on the ISO Standard 15839. The weekly water quality testing suite used in this study was taken from the ITA Report (ITA 1990). The protocol used included the following stages: preliminary response tests, routine tests, analyser performance indicators, and water quality variation (pH and conductivity).

An overview of all the individual tests and procedures that were used in this study can be found in the following sections. Residual disinfectant concentrations used in this evaluation are described as a percentage of the analyser working range. For free/total chlorine and monochloramine, this was 0-2 mg/L and for ammonia, a range of 0-1 mg/L (as NH$_3$-N) was used.

2.2 Preliminary response test
The preliminary response test (PRT) was conducted to determine the data logging frequency (see section 6.3.3 Data logging). The sample concentration in the analyser inlet stream was alternated between a low and high concentration (20% in tank A and 80% in tank B). The 20% solution was exposed to the analysers for a duration equivalent to at least 5 times the response time of the slowest analyser as indicated by the manufacturer’s specifications to ensure a stable reading was obtained. Then the analyser was exposed to the 80% solution for the same length of time.

Both samples (20 and 80% concentration) were measured using laboratory methods at the beginning and end of the runs to confirm that the residual concentration remained stable. Sample was run to waste at the start of a concentration change for a few seconds to prevent mixing of the 20% or 80% solution.

The PRT for each analyser was determined using results obtained from this test according to ISO standard 15839 (ISO 2003). The data logger was then set to scan the analyser output at frequency equivalent to 10% of the PRT. Each data point logged by the data logger consisted of the mean of ten consecutive readings made by the analyser. The logging frequency used was equivalent to the response time of the analyser having the fastest response time to ensure enough data points were collected.

2.3 Routine tests
A number of routine tests were undertaken and these are described in the following sections. Routine tests included: daily tests, weekly water quality analysis, and standard residual tests.

2.3.1 Daily tests
The following measurements were made on each day of testing: sample and ambient temperature; pH; the outlet flow of the analysers (only analysers equipped with overflow cell); standard residual test using a 35% standard calibration solution. Sample pH and temperatures were monitored continuously and logged using the data logger. Ambient temperature was measured using a mercury thermometer daily.
2.3.2 Weekly water quality analysis

A sampling and analysis program was undertaken in accordance with the schedule in Table 3.5 to identify any variation in source water quality. This schedule was based upon the ITA performance evaluation report (ITA 1990) for chlorine analysers.

Table 3.5 Water quality parameters.

<table>
<thead>
<tr>
<th>General</th>
<th>Metals</th>
<th>General</th>
<th>Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Aluminium</td>
<td>Nitrate</td>
<td>Iron</td>
</tr>
<tr>
<td>Alkalinity as CaCO₃</td>
<td>Barium</td>
<td>Nitrite</td>
<td>Lead</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Beryllium</td>
<td>Phosphorus</td>
<td>Manganese</td>
</tr>
<tr>
<td>Bromide</td>
<td>Boron</td>
<td>Sulphate</td>
<td>Nickel</td>
</tr>
<tr>
<td>Calcium</td>
<td>Cadmium</td>
<td>Sodium</td>
<td>Silver</td>
</tr>
<tr>
<td>Chloride</td>
<td>Chromium</td>
<td>Total Dissolved Solids</td>
<td>Strontium</td>
</tr>
<tr>
<td>Fluoride</td>
<td>Cobalt</td>
<td>Dissolved Organic Carbon</td>
<td>Vanadium</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Copper</td>
<td></td>
<td>Zinc</td>
</tr>
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</table>

Results of these analyses are presented in Table 3.6.
Table 3.6 Test rig feed water quality.

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<thead>
<tr>
<th>Test</th>
<th>Units</th>
<th>Week 1</th>
<th>Week 2</th>
<th>Week 3</th>
<th>Week 4</th>
<th>Week 5</th>
<th>Week 6</th>
<th>Week 7</th>
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<td>pH</td>
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<td>7.6</td>
<td>7.6</td>
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<td>7.4</td>
<td>7.3</td>
<td>7.6</td>
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<tr>
<td>Alkalinity</td>
<td>mg/L</td>
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<td>63.9</td>
<td>63.9</td>
<td>63.1</td>
<td>63.9</td>
<td>64.7</td>
<td>64.7</td>
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<td>Bicarbonate</td>
<td>mg/L</td>
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<td>78</td>
<td>76</td>
<td>77</td>
<td>78</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg/L</td>
<td>102</td>
<td>104</td>
<td>105</td>
<td>107</td>
<td>106</td>
<td>108</td>
<td>110</td>
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<tr>
<td>Fluoride</td>
<td>mg/L</td>
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<td>0.9</td>
<td>0.9</td>
<td>0.89</td>
<td>0.84</td>
<td>0.89</td>
<td>0.87</td>
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<td>Nitrate as N</td>
<td>mg/L</td>
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<td>0.393</td>
<td>0.398</td>
<td>0.402</td>
<td>0.374</td>
<td>0.353</td>
<td>0.372</td>
</tr>
<tr>
<td>Nitrite as N</td>
<td>mg/L</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
</tr>
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<td>Phosphorus Total</td>
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<td>&lt; 0.005</td>
<td>0.163</td>
<td>0.007</td>
<td>0.007</td>
<td>&lt; 0.005</td>
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<td>mg/L</td>
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<td>&lt; 0.10</td>
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<td>TDS</td>
<td>mg/L</td>
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<td>330</td>
<td>330</td>
<td>330</td>
<td>370</td>
<td>330</td>
<td>320</td>
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<tr>
<td>Conductivity</td>
<td>mg/L</td>
<td>576</td>
<td>592</td>
<td>602</td>
<td>599</td>
<td>671</td>
<td>599</td>
<td>590</td>
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<tr>
<td>Nitrate + Nitrite as N</td>
<td>mg/L</td>
<td>0.391</td>
<td>0.398</td>
<td>0.403</td>
<td>0.407</td>
<td>0.374</td>
<td>0.353</td>
<td>0.372</td>
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<td>mg/L</td>
<td>28.8</td>
<td>29.3</td>
<td>28.8</td>
<td>27.9</td>
<td>26.1</td>
<td>28.2</td>
<td>29.9</td>
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<td>Magnesium</td>
<td>mg/L</td>
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<td>15.3</td>
<td>15.5</td>
<td>15.5</td>
<td>16.1</td>
<td>15.9</td>
<td>17.1</td>
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<td>Sodium</td>
<td>mg/L</td>
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<td>60</td>
<td>60.8</td>
<td>61.2</td>
<td>62.6</td>
<td>60.7</td>
<td>61.8</td>
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<tr>
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<td>mg/L</td>
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<td>&lt; 0.02</td>
<td>0.039</td>
<td>0.041</td>
<td>0.051</td>
<td>0.043</td>
<td>0.035</td>
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<tr>
<td>Boron</td>
<td>mg/L</td>
<td>&lt; 0.040</td>
<td>0.04</td>
<td>&lt; 0.040</td>
<td>&lt; 0.040</td>
<td>&lt; 0.040</td>
<td>&lt; 0.040</td>
<td>&lt; 0.040</td>
</tr>
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<td>Cadmium</td>
<td>mg/L</td>
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<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
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<tr>
<td>Chromium</td>
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<td>0.003</td>
<td>&lt; 0.003</td>
<td>&lt; 0.003</td>
<td>&lt; 0.003</td>
<td>&lt; 0.003</td>
<td>&lt; 0.003</td>
</tr>
<tr>
<td>Cobalt</td>
<td>mg/L</td>
<td>&lt; 0.0005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
<td>&lt; 0.005</td>
</tr>
<tr>
<td>Copper</td>
<td>mg/L</td>
<td>0.039</td>
<td>0.142</td>
<td>0.112</td>
<td>0.032</td>
<td>0.051</td>
<td>0.162</td>
<td>0.173</td>
</tr>
<tr>
<td>Iron total</td>
<td>mg/L</td>
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<td>&lt; 0.030</td>
<td>&lt; 0.030</td>
<td>&lt; 0.030</td>
<td>&lt; 0.030</td>
<td>&lt; 0.030</td>
<td>&lt; 0.030</td>
</tr>
<tr>
<td>Lead</td>
<td>mg/L</td>
<td>0.0009</td>
<td>0.0045</td>
<td>0.0007</td>
<td>0.0006</td>
<td>0.0005</td>
<td>0.0005</td>
<td>0.0008</td>
</tr>
<tr>
<td>Manganese</td>
<td>mg/L</td>
<td>&lt; 0.0005</td>
<td>0.0008</td>
<td>0.0006</td>
<td>0.0006</td>
<td>0.0009</td>
<td>0.0014</td>
<td>0.0011</td>
</tr>
<tr>
<td>Nickel</td>
<td>mg/L</td>
<td>&lt; 0.0005</td>
<td>0.001</td>
<td>&lt; 0.0005</td>
<td>0.0007</td>
<td>0.0012</td>
<td>0.0005</td>
<td>0.0012</td>
</tr>
<tr>
<td>Silver</td>
<td>mg/L</td>
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<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
<td>&lt; 0.002</td>
</tr>
<tr>
<td>Zinc</td>
<td>mg/L</td>
<td>0.01</td>
<td>0.11</td>
<td>0.01</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
<td>0.009</td>
</tr>
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<td>Barium</td>
<td>mg/L</td>
<td>0.037</td>
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<td>0.0299</td>
<td>0.0313</td>
<td>0.0307</td>
<td>0.0351</td>
<td>0.0358</td>
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<tr>
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<td>mg/L</td>
<td>&lt; 0.0005</td>
<td>0.0005</td>
<td>&lt; 0.0005</td>
<td>0.0005</td>
<td>&lt; 0.0005</td>
<td>&lt; 0.0005</td>
<td>&lt; 0.0005</td>
</tr>
<tr>
<td>Strontium</td>
<td>mg/L</td>
<td>0.13</td>
<td>0.16</td>
<td>0.13</td>
<td>0.13</td>
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<td>0.16</td>
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<td>Vanadium</td>
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<td>0.004</td>
<td>0.005</td>
<td>0.004</td>
<td>0.004</td>
<td>&lt; 0.003</td>
<td>&lt; 0.003</td>
<td></td>
</tr>
</tbody>
</table>

2.3.3 Standard residual test

A 35% solution was prepared in tanks A or B and recirculated in the test rig using the distribution manifold to the online analysers and then returned to the tank. The analyser readings were allowed to stabilise before the sample residual concentration was confirmed using laboratory methods in triplicate. Measurements of residual concentration in the tank were made at regular intervals, normally at time equivalent to three response times of the slowest analyser. This test showed the general day-to-day performance of the analysers. By plotting the results in a response chart, any drift in the analyser reading can be determined. This allows calibration frequency to be determined, and also detect any analyser malfunctions.

2.4 Analyser performance indicators

A number of key analyser performance indicators were determined using the data obtained from tests previously described including: response, delay, rise and fall times; six day test (linearity, coefficient of variation, limit of detection, limit of quantification, repeatability, day-to-day repeatability, lowest detectable change, bias, short-term drift); memory effect; interference effect.

2.4.1 Response, delay, rise and fall times

The method used to determine response, delay, rise and fall time was similar to that used in the PRT test but the sample concentration supplied to analysers was alternated between 20% and 80% as
shown in Figure 3.1. The duration of each sample was equivalent to three times the response time of the analyser with the longest measuring interval through the recirculating system. This was repeated six times to obtain six comparable results for the positive and negative changes. The concentration of water actually supplied to the analysers after each tank change was confirmed using laboratory measurements.

![Figure 3.1 Sample concentration change for the response time test.](image)

### 2.4.2 Six day test

The six-day test (SDT) provided data to enable the determination of a number of analyser KPIs including: linearity; coefficient of variation; limit of detection; limit of quantification; repeatability; day-to-day repeatability; lowest detectable change; bias; and short-term drift. This test was carried out over six consecutive working days using a range of concentrations between 5 to 95% of the working range. Table 3.7 gives an overview of the concentrations used on different days. During this test, no adjustments or calibrations were made to the analysers unless they were capable of automatic calibration. The analysers were only calibrated before and after the SDT.

<table>
<thead>
<tr>
<th>Concentration 1, %</th>
<th>Day 1</th>
<th>Day 2</th>
<th>Day 3</th>
<th>Day 4</th>
<th>Day 5</th>
<th>Day 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration 2, %</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Concentration 3, %</td>
<td>95</td>
<td>65</td>
<td>50</td>
<td>65</td>
<td>65</td>
<td>65</td>
</tr>
</tbody>
</table>

Batches of water containing various disinfectant residual concentrations were prepared in the test rig tanks. In order to separate water samples with various residual disinfectant concentrations in analysers, the system was flushed with previously prepared de-chlorinated water (blank). The blank was always prepared by stirring tap water overnight to release the chlorine in water as described in the stand-by procedure. The blank was recirculated until all analyser readings reached zero for at least three response times of the slowest analyser.

Laboratory analysis was undertaken on samples taken from the test rig every 20 minutes (approximate) on water delivered to the analysers during the 6-days trial. Generally, three samples were taken for each concentration and chlorine and/or ammonia concentration were determined. The
blank was also tested in between changes in sample concentration to ensure contaminated did not occur.

Figure 3.2 shows a series of sample concentration changes separated by the blanks made during day 2 of the SDT. It can be seen that three different concentrations equivalent to 5, 35, and 65% of the measuring range were used. The SDT was repeated after the memory effect test described in the following section, to provide a duplicate set of data.

**2.4.3 Memory effect**

In order to determine any memory effect exhibited by an analyser, the analysers were first exposed to a sample having a high concentration and then to a low concentration. An analyser having a memory effect would continue to display an output at the higher concentration and not drop back to the lower concentration when exposed to the low concentration. Figure 3.3 presents a series of changes made to concentration sample exposed to the analysers during this test. Two solutions, equivalent to 20 and 200%, were prepared in the tank A and B. The 200% solution was recycled for a period equivalent to five response times of the slowest analyser before it was switched to the 20% concentration. This cycle was repeated six times. During this experiment, measurement of analyser sample chlorine and ammonia concentration was regularly undertaken to confirmation that the correct concentration was achieved.

**Figure 3.3** Schematic development of concentration change for memory effect trial.
2.5 Water quality variation
The impact of water quality variation (pH and conductivity) and on analyser performance was investigated.

2.5.1 pH
Analysers were exposed to a 50% concentration sample and the pH was varied from pH 5 to pH 10 using sulphuric acid and sodium hydroxide solution addition respectively to achieve several pH conditions. For each pH condition, the analyser reading was allowed to stabilise and two measurements of the total chlorine or ammonia concentration were made (Figure 3.4). The first measurement was taken after 15 minutes and the second after 30 minutes. This procedure was repeated for a range in pH from pH 5 to 10.

2.5.2 Conductivity
The impact of variation in sample conductivity for the range 250 to 850 µS/cm was investigated. Low conductivity water was prepared by blending de-chlorinated tap water with distilled water and mixing in one of the test rig tanks to achieve a conductivity of 250 µS/cm. This was then spiked with chlorine or ammonia solution to achieve a concentration equivalent to 50% of the working range. The conductivity of the water in the tank was then confirmed and adjusted if necessary. Low conductivity water was then recirculated to the analysers. When the analyser readings had stabilised, the chlorine or ammonia residual concentration of the sample was determined using a titration or colorimetric method. A repeat measurement was taken 15 minutes later as per the pH test. This method was repeated for water having a conductivity of 500 and 850 µS/cm by adding concentrated potassium chloride solution.

![Figure 3.4 Conditions used during pH variation test.](image-url)
3 RESULTS AND DISCUSSION

This chapter presents experimental data and calculated results for free chlorine, total chlorine/monochloramine and ammonia analysers obtained during laboratory evaluation trials.

3.1 Free chlorine analysers

In this section, free chlorine analysers are labelled as follows:

- Prominent – Dulcotest Sensor Type CLE
- Prominent – Dulcometer D1C
- ATI Model A 15/62
- Endress & Houser CCS141
- B & C Electronics CL 7685
- Yokogawa Model FC400G-63*A/Z
- Hach CL17
- Wallace & Tiernan – Depolox 3 plus (membrane style)
- Wallace & Tiernan – Depolox 3 plus (bare electrode style)

Free chlorine analyser performance indicators are presented in the following section.

3.1.1 Response, delay, rise and fall times

Tables 3.8 and 3.9 summarise average values for positive and negative response times, delay times, rise and fall times of free chlorine analysers. Each value is an average result of 6 measurements.

### Table 3.8 Average values of performance characteristics.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Analyser Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Response time for positive change, ( t_{\text{Response}^+} ), sec</td>
<td>81.2</td>
</tr>
<tr>
<td>Delay time for positive change, ( t_{\text{Delay}^+} ), sec</td>
<td>20.7</td>
</tr>
<tr>
<td>Response time for positive change, ( t_{\text{Response}^-} ), sec</td>
<td>91.6</td>
</tr>
<tr>
<td>Delay time for negative change, ( t_{\text{Delay}^-} ), sec</td>
<td>19.7</td>
</tr>
<tr>
<td>Rise time, sec</td>
<td>60.6</td>
</tr>
<tr>
<td>Fall time, sec</td>
<td>71.9</td>
</tr>
</tbody>
</table>

### Table 3.9 Average values of performance characteristics.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Analyser Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Response time for positive change, ( t_{\text{Response}^+} ), sec</td>
<td>59.9</td>
</tr>
<tr>
<td>Delay time for positive change, ( t_{\text{Delay}^+} ), sec</td>
<td>15.8</td>
</tr>
<tr>
<td>Response time for positive change, ( t_{\text{Response}^-} ), sec</td>
<td>48.4</td>
</tr>
<tr>
<td>Delay time for negative change, ( t_{\text{Delay}^-} ), sec</td>
<td>12.2</td>
</tr>
<tr>
<td>Rise time, sec</td>
<td>44.1</td>
</tr>
<tr>
<td>Fall time, sec</td>
<td>36.1</td>
</tr>
</tbody>
</table>
3.1.2 Linearity

Table 3.10 presents linearity results for the 9 free chlorine analysers that were evaluated in this study for samples containing 5-95% of the measurement range.

<table>
<thead>
<tr>
<th>Titre</th>
<th>Chlorine Concentration for Analyser number</th>
</tr>
</thead>
<tbody>
<tr>
<td>x_i  %</td>
<td>1</td>
</tr>
<tr>
<td>mg/L</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.15</td>
</tr>
<tr>
<td>20</td>
<td>0.40</td>
</tr>
<tr>
<td>35</td>
<td>0.67</td>
</tr>
<tr>
<td>50</td>
<td>0.99</td>
</tr>
<tr>
<td>65</td>
<td>1.30</td>
</tr>
<tr>
<td>80</td>
<td>1.56</td>
</tr>
<tr>
<td>95</td>
<td>1.85</td>
</tr>
</tbody>
</table>

Table 3.11 shows the R^2 value (Pearson coefficient) for individual free chlorine analysers and laboratory analysis.

<table>
<thead>
<tr>
<th>Analyser number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eq.</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>----</td>
</tr>
<tr>
<td>0.795x</td>
</tr>
<tr>
<td>R^2</td>
</tr>
<tr>
<td>0.8730</td>
</tr>
</tbody>
</table>

Figures 3.5 to 3.13 present individual analyser free chlorine measurement results versus laboratory results.

**Figure 3.5** Linearity test for analyser 1  
**Figure 3.6** Linearity test for analyser 2
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL WITHIN DISTRIBUTION SYSTEMS

Figure 3.7 Linearity test for analyser 3

Figure 3.8 Linearity test for analyser 4

Figure 3.9 Linearity test for analyser 5

Figure 3.10 Linearity test for analyser 6

Figure 3.11 Linearity test for analyser 7

Figure 3.12 Linearity test for analyser 8
3.1.3 Coefficient of variation

Table 3.12 presents coefficient of variation results for the free chlorine analysers evaluated in this study.

<table>
<thead>
<tr>
<th>Coefficient of Variation for analyser</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
</tr>
<tr>
<td>0.34</td>
<td>0.16</td>
<td>0.27</td>
<td>0.22</td>
<td>0.27</td>
<td>0.14</td>
<td>0.15</td>
<td>0.61</td>
<td>0.56</td>
<td></td>
</tr>
</tbody>
</table>
3.1.4 Limit of detection and limit of quantification

Limit of detection (LOD, mg/L) and limit of quantification results for the free chlorine analyser evaluated in this study determined at a concentration equivalent to 5% (nominal) of the measuring range (0.11-0.15 mg/L) are presented in Table 3.13.

Table 3.13 Free chlorine analyser limit of LOD and LOQ

<table>
<thead>
<tr>
<th>Titration Results</th>
<th>mg/L</th>
<th>0.14</th>
<th>0.15</th>
<th>0.15</th>
<th>0.13</th>
<th>0.11</th>
<th>Std. Dev., mg/L</th>
<th>LOD, mg/L</th>
<th>LOQ, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>0.17</td>
<td>0.16</td>
<td>0.15</td>
<td>0.14</td>
<td>0.12</td>
<td>0.11</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>0.14</td>
<td>0.13</td>
<td>0.11</td>
<td>0.10</td>
<td>0.08</td>
<td>0.07</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>0.02</td>
<td>0.01</td>
<td>-0.01</td>
<td>-0.02</td>
<td>-0.05</td>
<td>-0.06</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>0.22</td>
<td>0.21</td>
<td>0.20</td>
<td>0.19</td>
<td>0.17</td>
<td>0.16</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>0.23</td>
<td>0.21</td>
<td>0.20</td>
<td>0.18</td>
<td>0.16</td>
<td>0.15</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>0.29</td>
<td>0.27</td>
<td>0.26</td>
<td>0.25</td>
<td>0.24</td>
<td>0.23</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>Analyser - 7</td>
<td>mg/L</td>
<td>0.16</td>
<td>0.19</td>
<td>0.18</td>
<td>0.17</td>
<td>0.15</td>
<td>0.14</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>Analyser - 8</td>
<td>mg/L</td>
<td>0.09</td>
<td>0.08</td>
<td>0.08</td>
<td>0.07</td>
<td>0.07</td>
<td>0.06</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Analyser - 9</td>
<td>mg/L</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

3.1.5 Repeatability and day-to-day repeatability

Tables 3.14 and 3.15 show repeatability results (RPT, mg/L) for free chlorine analysers at 20 and 80% of the measuring range.

Table 3.14 Free chlorine analyser RPT results at 20% of the measuring range

<table>
<thead>
<tr>
<th>Titration Results</th>
<th>mg/L</th>
<th>0.41</th>
<th>0.41</th>
<th>0.40</th>
<th>0.40</th>
<th>0.39</th>
<th>0.37</th>
<th>RPT, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>0.49</td>
<td>0.45</td>
<td>0.42</td>
<td>0.40</td>
<td>0.37</td>
<td>0.35</td>
<td>0.05</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>0.38</td>
<td>0.37</td>
<td>0.36</td>
<td>0.37</td>
<td>0.35</td>
<td>0.34</td>
<td>0.01</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>0.45</td>
<td>0.42</td>
<td>0.39</td>
<td>0.37</td>
<td>0.35</td>
<td>0.33</td>
<td>0.05</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>0.58</td>
<td>0.56</td>
<td>0.54</td>
<td>0.52</td>
<td>0.50</td>
<td>0.48</td>
<td>0.04</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>0.64</td>
<td>0.60</td>
<td>0.56</td>
<td>0.53</td>
<td>0.50</td>
<td>0.47</td>
<td>0.06</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>0.51</td>
<td>0.49</td>
<td>0.48</td>
<td>0.46</td>
<td>0.45</td>
<td>0.44</td>
<td>0.03</td>
</tr>
<tr>
<td>Analyser - 7</td>
<td>mg/L</td>
<td>0.44</td>
<td>0.43</td>
<td>0.42</td>
<td>0.41</td>
<td>0.40</td>
<td>0.39</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 8</td>
<td>mg/L</td>
<td>0.21</td>
<td>0.20</td>
<td>0.19</td>
<td>0.18</td>
<td>0.17</td>
<td>0.16</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 9</td>
<td>mg/L</td>
<td>0.19</td>
<td>0.17</td>
<td>0.15</td>
<td>0.14</td>
<td>0.13</td>
<td>0.12</td>
<td>0.03</td>
</tr>
</tbody>
</table>
### Table 3.15 Free chlorine analyser RPT results at 80% of the measuring range

<table>
<thead>
<tr>
<th>Titration Results</th>
<th>mg/L</th>
<th>1.60</th>
<th>1.58</th>
<th>1.55</th>
<th>1.55</th>
<th>1.54</th>
<th>1.54</th>
<th>RPT, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>1.00</td>
<td>1.00</td>
<td>0.98</td>
<td>0.97</td>
<td>0.95</td>
<td>0.94</td>
<td>0.03</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>1.52</td>
<td>1.59</td>
<td>1.65</td>
<td>1.68</td>
<td>1.71</td>
<td>1.72</td>
<td>0.08</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>1.68</td>
<td>1.66</td>
<td>1.64</td>
<td>1.63</td>
<td>1.61</td>
<td>1.59</td>
<td>0.03</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>1.46</td>
<td>1.50</td>
<td>1.51</td>
<td>1.51</td>
<td>1.51</td>
<td>1.50</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>1.50</td>
<td>1.49</td>
<td>1.47</td>
<td>1.46</td>
<td>1.44</td>
<td>1.43</td>
<td>0.03</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>1.54</td>
<td>1.55</td>
<td>1.54</td>
<td>1.54</td>
<td>1.54</td>
<td>1.53</td>
<td>0.01</td>
</tr>
<tr>
<td>Analyser - 7</td>
<td>mg/L</td>
<td>1.49</td>
<td>1.61</td>
<td>1.60</td>
<td>1.58</td>
<td>1.58</td>
<td>1.57</td>
<td>0.04</td>
</tr>
<tr>
<td>Analyser - 8</td>
<td>mg/L</td>
<td>0.60</td>
<td>0.59</td>
<td>0.59</td>
<td>0.58</td>
<td>0.58</td>
<td>0.58</td>
<td>0.01</td>
</tr>
<tr>
<td>Analyser - 9</td>
<td>mg/L</td>
<td>0.67</td>
<td>0.66</td>
<td>0.65</td>
<td>0.64</td>
<td>0.63</td>
<td>0.63</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Results for free chlorine analyser day-to-day repeatability at 35% and 65% of the measuring range are given in Tables 3.16 and 3.17.

### Table 3.16 Free chlorine analyser repeatability results at 35% of the measuring range

<table>
<thead>
<tr>
<th>Titration Results</th>
<th>mg/L</th>
<th>0.67</th>
<th>0.68</th>
<th>0.67</th>
<th>0.69</th>
<th>0.72</th>
<th>0.70</th>
<th>Std. Dev., mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>0.67</td>
<td>0.75</td>
<td>0.69</td>
<td>0.60</td>
<td>0.54</td>
<td>0.52</td>
<td>0.09</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>0.65</td>
<td>0.53</td>
<td>0.71</td>
<td>0.65</td>
<td>0.65</td>
<td>0.66</td>
<td>0.06</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>0.61</td>
<td>0.77</td>
<td>0.27</td>
<td>0.81</td>
<td>0.75</td>
<td>0.74</td>
<td>0.20</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>0.65</td>
<td>0.75</td>
<td>0.63</td>
<td>0.78</td>
<td>0.69</td>
<td>0.74</td>
<td>0.06</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>0.63</td>
<td>0.95</td>
<td>0.69</td>
<td>0.86</td>
<td>0.75</td>
<td>0.76</td>
<td>0.12</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>0.80</td>
<td>0.75</td>
<td>0.28</td>
<td>0.85</td>
<td>0.79</td>
<td>0.79</td>
<td>0.21</td>
</tr>
<tr>
<td>Analyser - 7</td>
<td>mg/L</td>
<td>0.66</td>
<td>0.62</td>
<td>0.81</td>
<td>0.75</td>
<td>0.75</td>
<td>0.74</td>
<td>0.07</td>
</tr>
<tr>
<td>Analyser - 8</td>
<td>mg/L</td>
<td>0.67</td>
<td>0.31</td>
<td>0.53</td>
<td>0.30</td>
<td>0.29</td>
<td>0.70</td>
<td>0.19</td>
</tr>
<tr>
<td>Analyser - 9</td>
<td>mg/L</td>
<td>0.67</td>
<td>0.34</td>
<td>0.71</td>
<td>0.28</td>
<td>0.29</td>
<td>0.78</td>
<td>0.23</td>
</tr>
</tbody>
</table>

### Table 3.17 Free chlorine analyser repeatability results at 65% of the measuring range

<table>
<thead>
<tr>
<th>Titration Results</th>
<th>mg/L</th>
<th>-</th>
<th>1.30</th>
<th>1.28</th>
<th>1.26</th>
<th>1.24</th>
<th>1.26</th>
<th>Std. Dev., mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>-</td>
<td>1.15</td>
<td>1.28</td>
<td>0.91</td>
<td>0.84</td>
<td>0.85</td>
<td>0.20</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>-</td>
<td>1.26</td>
<td>1.46</td>
<td>1.18</td>
<td>1.25</td>
<td>1.23</td>
<td>0.11</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>-</td>
<td>1.42</td>
<td>0.53</td>
<td>1.42</td>
<td>1.33</td>
<td>1.37</td>
<td>0.38</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>-</td>
<td>1.32</td>
<td>1.08</td>
<td>Table 1</td>
<td>1.19</td>
<td>1.25</td>
<td>0.11</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>-</td>
<td>1.47</td>
<td>1.54</td>
<td>1.32</td>
<td>1.24</td>
<td>1.34</td>
<td>0.12</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>-</td>
<td>1.29</td>
<td>0.59</td>
<td>1.35</td>
<td>1.25</td>
<td>1.24</td>
<td>0.31</td>
</tr>
<tr>
<td>Analyser - 7</td>
<td>mg/L</td>
<td>-</td>
<td>1.17</td>
<td>1.43</td>
<td>1.27</td>
<td>1.28</td>
<td>1.28</td>
<td>0.09</td>
</tr>
<tr>
<td>Analyser - 8</td>
<td>mg/L</td>
<td>-</td>
<td>0.52</td>
<td>1.26</td>
<td>0.50</td>
<td>0.48</td>
<td>1.20</td>
<td>0.40</td>
</tr>
<tr>
<td>Analyser - 9</td>
<td>mg/L</td>
<td>-</td>
<td>0.60</td>
<td>1.25</td>
<td>0.48</td>
<td>0.52</td>
<td>1.47</td>
<td>0.46</td>
</tr>
</tbody>
</table>
### 3.1.6 Lowest detectable change

Lowest detectable change results for free chlorine analysers are given in Tables 3.18 and 3.19 for 3.20 and 80% of the measuring range.

#### Table 3.18 Free chlorine analyser LDC results at 20% of the measuring range

<table>
<thead>
<tr>
<th>Titration Results</th>
<th>mg/L</th>
<th>0.41</th>
<th>0.41</th>
<th>0.40</th>
<th>0.39</th>
<th>0.37</th>
<th>LDC, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>0.49</td>
<td>0.45</td>
<td>0.42</td>
<td>0.40</td>
<td>0.37</td>
<td>0.35</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>0.38</td>
<td>0.37</td>
<td>0.36</td>
<td>0.37</td>
<td>0.35</td>
<td>0.34</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>0.45</td>
<td>0.42</td>
<td>0.39</td>
<td>0.37</td>
<td>0.35</td>
<td>0.33</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>0.58</td>
<td>0.56</td>
<td>0.54</td>
<td>0.52</td>
<td>0.50</td>
<td>0.48</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>0.64</td>
<td>0.60</td>
<td>0.56</td>
<td>0.53</td>
<td>0.50</td>
<td>0.47</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>0.51</td>
<td>0.49</td>
<td>0.48</td>
<td>0.46</td>
<td>0.45</td>
<td>0.44</td>
</tr>
<tr>
<td>Analyser - 7</td>
<td>mg/L</td>
<td>0.44</td>
<td>0.43</td>
<td>0.42</td>
<td>0.41</td>
<td>0.40</td>
<td>0.39</td>
</tr>
<tr>
<td>Analyser - 8</td>
<td>mg/L</td>
<td>0.21</td>
<td>0.20</td>
<td>0.19</td>
<td>0.18</td>
<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td>Analyser - 9</td>
<td>mg/L</td>
<td>0.19</td>
<td>0.17</td>
<td>0.15</td>
<td>0.14</td>
<td>0.13</td>
<td>0.12</td>
</tr>
</tbody>
</table>

#### Table 3.19 Free chlorine analyser LDC results at 80% of the measuring range

<table>
<thead>
<tr>
<th>Titration Results</th>
<th>mg/L</th>
<th>1.60</th>
<th>1.58</th>
<th>1.55</th>
<th>1.55</th>
<th>1.54</th>
<th>1.54</th>
<th>LDC, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>1.00</td>
<td>1.00</td>
<td>0.98</td>
<td>0.97</td>
<td>0.95</td>
<td>0.94</td>
<td>0.08</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>1.52</td>
<td>1.59</td>
<td>1.65</td>
<td>1.68</td>
<td>1.71</td>
<td>1.72</td>
<td>0.23</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>1.68</td>
<td>1.66</td>
<td>1.64</td>
<td>1.63</td>
<td>1.61</td>
<td>1.59</td>
<td>0.10</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>1.46</td>
<td>1.50</td>
<td>1.51</td>
<td>1.51</td>
<td>1.51</td>
<td>1.50</td>
<td>0.06</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>1.50</td>
<td>1.49</td>
<td>1.47</td>
<td>1.46</td>
<td>1.44</td>
<td>1.43</td>
<td>0.08</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>1.54</td>
<td>1.55</td>
<td>1.54</td>
<td>1.54</td>
<td>1.54</td>
<td>1.53</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 7</td>
<td>mg/L</td>
<td>1.49</td>
<td>1.61</td>
<td>1.60</td>
<td>1.58</td>
<td>1.58</td>
<td>1.57</td>
<td>0.13</td>
</tr>
<tr>
<td>Analyser - 8</td>
<td>mg/L</td>
<td>0.60</td>
<td>0.59</td>
<td>0.59</td>
<td>0.58</td>
<td>0.58</td>
<td>0.58</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 9</td>
<td>mg/L</td>
<td>0.67</td>
<td>0.66</td>
<td>0.65</td>
<td>0.64</td>
<td>0.63</td>
<td>0.63</td>
<td>0.05</td>
</tr>
</tbody>
</table>
3.1.7 Bias

Bias results for the free chlorine residual analyses evaluated in this study are given in Tables 3.20 and 3.21 for 20% and 80% of the measuring range, respectively.

Table 3.20 Free chlorine analyser bias results at 20% of the measuring range

<table>
<thead>
<tr>
<th>Titration Results</th>
<th>mg/L</th>
<th>0.41</th>
<th>0.41</th>
<th>0.40</th>
<th>0.40</th>
<th>0.39</th>
<th>0.37</th>
<th>Bias, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>0.49</td>
<td>0.45</td>
<td>0.42</td>
<td>0.40</td>
<td>0.37</td>
<td>0.35</td>
<td>0.01</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>0.38</td>
<td>0.37</td>
<td>0.36</td>
<td>0.37</td>
<td>0.35</td>
<td>0.34</td>
<td>-0.04</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>0.45</td>
<td>0.42</td>
<td>0.39</td>
<td>0.37</td>
<td>0.35</td>
<td>0.33</td>
<td>-0.01</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>0.58</td>
<td>0.56</td>
<td>0.54</td>
<td>0.52</td>
<td>0.50</td>
<td>0.48</td>
<td>0.13</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>0.64</td>
<td>0.60</td>
<td>0.56</td>
<td>0.53</td>
<td>0.50</td>
<td>0.47</td>
<td>0.15</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>0.51</td>
<td>0.49</td>
<td>0.48</td>
<td>0.46</td>
<td>0.45</td>
<td>0.44</td>
<td>0.07</td>
</tr>
<tr>
<td>Analyser - 7</td>
<td>mg/L</td>
<td>0.44</td>
<td>0.43</td>
<td>0.42</td>
<td>0.41</td>
<td>0.40</td>
<td>0.39</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 8</td>
<td>mg/L</td>
<td>0.21</td>
<td>0.20</td>
<td>0.19</td>
<td>0.18</td>
<td>0.17</td>
<td>0.16</td>
<td>-0.21</td>
</tr>
<tr>
<td>Analyser - 9</td>
<td>mg/L</td>
<td>0.19</td>
<td>0.17</td>
<td>0.15</td>
<td>0.14</td>
<td>0.13</td>
<td>0.12</td>
<td>-0.25</td>
</tr>
</tbody>
</table>

Table 3.21 Free chlorine analyser bias results at 80% of the measuring range

<table>
<thead>
<tr>
<th>Titration Results</th>
<th>mg/L</th>
<th>1.60</th>
<th>1.58</th>
<th>1.55</th>
<th>1.55</th>
<th>1.54</th>
<th>1.54</th>
<th>Bias, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>1.00</td>
<td>1.00</td>
<td>0.98</td>
<td>0.97</td>
<td>0.95</td>
<td>0.94</td>
<td>-0.59</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>1.52</td>
<td>1.59</td>
<td>1.65</td>
<td>1.68</td>
<td>1.71</td>
<td>1.72</td>
<td>0.09</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>1.68</td>
<td>1.66</td>
<td>1.64</td>
<td>1.63</td>
<td>1.61</td>
<td>1.59</td>
<td>0.07</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>1.46</td>
<td>1.50</td>
<td>1.51</td>
<td>1.51</td>
<td>1.51</td>
<td>1.50</td>
<td>-0.06</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>1.50</td>
<td>1.49</td>
<td>1.47</td>
<td>1.46</td>
<td>1.44</td>
<td>1.43</td>
<td>-0.09</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>1.54</td>
<td>1.55</td>
<td>1.54</td>
<td>1.54</td>
<td>1.54</td>
<td>1.53</td>
<td>-0.02</td>
</tr>
<tr>
<td>Analyser - 7</td>
<td>mg/L</td>
<td>1.49</td>
<td>1.61</td>
<td>1.60</td>
<td>1.58</td>
<td>1.58</td>
<td>1.57</td>
<td>0.01</td>
</tr>
<tr>
<td>Analyser - 8</td>
<td>mg/L</td>
<td>0.60</td>
<td>0.59</td>
<td>0.59</td>
<td>0.58</td>
<td>0.58</td>
<td>0.58</td>
<td>-0.97</td>
</tr>
<tr>
<td>Analyser - 9</td>
<td>mg/L</td>
<td>0.67</td>
<td>0.66</td>
<td>0.65</td>
<td>0.64</td>
<td>0.63</td>
<td>0.63</td>
<td>-0.91</td>
</tr>
</tbody>
</table>

3.1.8 Short-term drift

Free chlorine analyser short-term drift results are given in Table 3.22. It was not possible to keep free chlorine concentration at 50% of the measurement range in the laboratory solution for a 24 hour period. Therefore, the short-term drift experiment was carried for a period of about 2.5 hours, and short-term drift was calculated as the slope of regression line expressed in % of measuring range.
Table 3.22 Free chlorine analyser ShTD tests results at 50% of the measuring range

<table>
<thead>
<tr>
<th>Time</th>
<th>min</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>1.03</td>
<td>1.03</td>
<td>1.04</td>
<td>1.03</td>
<td>1.03</td>
<td>1.03</td>
<td>1.03</td>
<td>1.03</td>
<td>1.03</td>
<td>1.03</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>0.94</td>
<td>0.94</td>
<td>0.94</td>
<td>0.93</td>
<td>0.93</td>
<td>0.93</td>
<td>0.93</td>
<td>0.93</td>
<td>0.93</td>
<td>0.92</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>1.26</td>
<td>1.26</td>
<td>1.26</td>
<td>1.25</td>
<td>1.25</td>
<td>1.24</td>
<td>1.24</td>
<td>1.23</td>
<td>1.23</td>
<td>1.23</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>0.49</td>
<td>0.49</td>
<td>0.49</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>Analyser - 7</td>
<td>mg/L</td>
<td>1.24</td>
<td>1.24</td>
<td>1.24</td>
<td>1.23</td>
<td>1.23</td>
<td>1.23</td>
<td>1.22</td>
<td>1.22</td>
<td>1.21</td>
<td>1.22</td>
</tr>
<tr>
<td>Analyser - 8</td>
<td>mg/L</td>
<td>0.93</td>
<td>0.94</td>
<td>0.93</td>
<td>0.94</td>
<td>0.95</td>
<td>0.95</td>
<td>0.94</td>
<td>0.95</td>
<td>0.96</td>
<td>0.97</td>
</tr>
<tr>
<td>Analyser - 9</td>
<td>mg/L</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1.04</td>
<td>1.04</td>
<td>1.03</td>
<td>1.03</td>
<td>1.03</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Table 3.22 (continued) Free chlorine analyser ShTD tests results at 50% of the measuring range

<table>
<thead>
<tr>
<th>Time</th>
<th>min</th>
<th>100</th>
<th>110</th>
<th>120</th>
<th>130</th>
<th>140</th>
<th>Slope, (mg/L)/hour</th>
<th>ShTD, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>1.03</td>
<td>1.02</td>
<td>1.02</td>
<td>1.02</td>
<td>1.02</td>
<td>-0.0058</td>
<td>-0.29</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
<td>1.15</td>
<td>0.0004</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>0.43</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
<td>-0.0047</td>
<td>-0.24</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>0.92</td>
<td>0.91</td>
<td>0.91</td>
<td>0.91</td>
<td>0.91</td>
<td>-0.0144</td>
<td>-0.72</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>1.23</td>
<td>1.22</td>
<td>1.22</td>
<td>1.21</td>
<td>1.21</td>
<td>-0.0214</td>
<td>-1.07</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>0.48</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>-0.0086</td>
<td>-0.43</td>
</tr>
<tr>
<td>Analyser - 7</td>
<td>mg/L</td>
<td>1.21</td>
<td>1.20</td>
<td>1.19</td>
<td>1.19</td>
<td>1.19</td>
<td>-0.0234</td>
<td>-1.17</td>
</tr>
<tr>
<td>Analyser - 8</td>
<td>mg/L</td>
<td>0.97</td>
<td>0.97</td>
<td>0.98</td>
<td>0.98</td>
<td>0.97</td>
<td>0.0216</td>
<td>1.08</td>
</tr>
<tr>
<td>Analyser - 9</td>
<td>mg/L</td>
<td>1.03</td>
<td>1.03</td>
<td>1.02</td>
<td>1.02</td>
<td>1.02</td>
<td>-0.0146</td>
<td>-0.73</td>
</tr>
</tbody>
</table>

3.1.9 Memory effect

Memory effect results for free chlorine analysers are presented in Table 3.23. The memory effect is calculated as the difference between the mean value of six measurements made using the laboratory method and the online analyser (Table 3.24). If the calculated value is bigger than the lowest detectable change, then the monitor is said to have a memory effect.

Table 3.23 Free chlorine analyser memory effects tests results at 20% of the measuring range

<table>
<thead>
<tr>
<th>Titration mg/L</th>
<th>Readings from Analyser, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0.53</td>
<td>0.61</td>
</tr>
<tr>
<td>0.53</td>
<td>0.56</td>
</tr>
<tr>
<td>0.48</td>
<td>0.46</td>
</tr>
<tr>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>0.49</td>
<td>0.45</td>
</tr>
<tr>
<td>0.45</td>
<td>0.52</td>
</tr>
<tr>
<td>Average</td>
<td>0.51</td>
</tr>
</tbody>
</table>
Table 3.24 Summary of free chlorine analyser memory effects.

| Lowest detectable change at 20 % of the measuring range for free chlorine analysers, mg/L |
|-----------------------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 1    | 2       | 3       | 4       | 5       | 6       | 7       | 8       | 9       |
| 0.15 | 0.04    | 0.14    | 0.12    | 0.19    | 0.08    | 0.06    | 0.06    | 0.08    |

| Difference between 6 laboratory measurements and 6 online free chlorine analyser, mg/L |
|-----------------------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| 1    | 2       | 3       | 4       | 5       | 6       | 7       | 8       | 9       |
| 0.02 | 0.04    | 0.00    | 0.16    | 0.04    | 0.06    | 0.05    | 0.06    | -0.05   |

<table>
<thead>
<tr>
<th>Memory effect for analyser, (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
</tr>
</tbody>
</table>

3.1.10 Interferences

Tables 3.25 to 3.30 compare results obtained using laboratory analysis versus online free chlorine analysers in the presence of various potential interference parameters.

Table 3.25 Free chlorine analyser pH interference test results

<table>
<thead>
<tr>
<th>pH</th>
<th>Titration Results mg/L</th>
<th>Chlorine readings from analysers (mg/L)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>j</td>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>0.99</td>
<td></td>
<td>2.00</td>
<td>0.66</td>
<td>1.67</td>
<td>1.03</td>
<td>1.94</td>
<td>0.95</td>
<td>1.04</td>
</tr>
<tr>
<td>6</td>
<td>1.04</td>
<td></td>
<td>2.00</td>
<td>0.70</td>
<td>1.75</td>
<td>1.12</td>
<td>1.82</td>
<td>0.97</td>
<td>1.07</td>
</tr>
<tr>
<td>7</td>
<td>0.94</td>
<td></td>
<td>1.85</td>
<td>0.82</td>
<td>1.40</td>
<td>1.13</td>
<td>1.16</td>
<td>0.86</td>
<td>0.97</td>
</tr>
<tr>
<td>8</td>
<td>1.04</td>
<td></td>
<td>1.31</td>
<td>1.14</td>
<td>1.14</td>
<td>1.46</td>
<td>0.87</td>
<td>0.99</td>
<td>1.06</td>
</tr>
<tr>
<td>9</td>
<td>1.03</td>
<td></td>
<td>0.59</td>
<td>0.43</td>
<td>0.66</td>
<td>1.22</td>
<td>0.33</td>
<td>1.09</td>
<td>1.03</td>
</tr>
<tr>
<td>10</td>
<td>0.97</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.11</td>
<td>0.02</td>
<td>0.72</td>
<td>0.98</td>
</tr>
<tr>
<td>% of Span</td>
<td>100.2</td>
<td>33.1</td>
<td>83.4</td>
<td>46.1</td>
<td>96.1</td>
<td>11.8</td>
<td>3.3</td>
<td>44.6</td>
<td>186.3</td>
</tr>
</tbody>
</table>

Table 3.26 Free chlorine analyser electrolytic conductivity interference test results

<table>
<thead>
<tr>
<th>Conductivity uS/cm</th>
<th>Titration Results mg/L</th>
<th>Chlorine readings from analysers (mg/L)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>286</td>
<td>0.97</td>
<td></td>
<td>0.71</td>
<td>1.04</td>
<td>0.83</td>
<td>0.95</td>
<td>0.77</td>
<td>0.91</td>
<td>0.96</td>
<td>0.98</td>
</tr>
<tr>
<td>572</td>
<td>1.03</td>
<td></td>
<td>0.74</td>
<td>1.05</td>
<td>0.89</td>
<td>0.96</td>
<td>0.82</td>
<td>1.15</td>
<td>0.88</td>
<td>0.92</td>
</tr>
<tr>
<td>819</td>
<td>0.99</td>
<td></td>
<td>0.72</td>
<td>1.10</td>
<td>0.86</td>
<td>0.99</td>
<td>0.82</td>
<td>1.20</td>
<td>0.92</td>
<td>0.92</td>
</tr>
<tr>
<td>% of Span</td>
<td>1.5</td>
<td>2.7</td>
<td>3.0</td>
<td>2.3</td>
<td>2.5</td>
<td>14.1</td>
<td>4.1</td>
<td>2.8</td>
<td>4.8</td>
<td></td>
</tr>
</tbody>
</table>
### Table 3.27 Free chlorine analyser iron concentration interference test results

<table>
<thead>
<tr>
<th>Iron mg/L</th>
<th>Titration Results mg/L</th>
<th>Chlorine readings from analysers (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0.35</td>
<td>1.00</td>
<td>1.03</td>
</tr>
<tr>
<td>0.26</td>
<td>0.97</td>
<td>1.12</td>
</tr>
<tr>
<td>0.13</td>
<td>1.02</td>
<td>1.09</td>
</tr>
<tr>
<td>% of Span</td>
<td></td>
<td>4.8</td>
</tr>
</tbody>
</table>

### Table 3.28 Manganese concentration interference test results

<table>
<thead>
<tr>
<th>Manganese mg/L</th>
<th>Titration Results mg/L</th>
<th>Chlorine readings from analysers (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0.147</td>
<td>1.01</td>
<td>0.56</td>
</tr>
<tr>
<td>0.077</td>
<td>0.96</td>
<td>0.53</td>
</tr>
<tr>
<td>0.062</td>
<td>0.97</td>
<td>0.49</td>
</tr>
<tr>
<td>% of Span</td>
<td></td>
<td>3.4</td>
</tr>
</tbody>
</table>

### Table 3.29 Temperature interference test results

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Titration Results mg/L</th>
<th>Chlorine readings from analysers (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>21</td>
<td>0.99</td>
<td>0.45</td>
</tr>
<tr>
<td>25</td>
<td>1.00</td>
<td>0.43</td>
</tr>
<tr>
<td>30</td>
<td>0.99</td>
<td>0.43</td>
</tr>
<tr>
<td>35</td>
<td>0.98</td>
<td>0.40</td>
</tr>
<tr>
<td>39</td>
<td>1.00</td>
<td>0.34</td>
</tr>
<tr>
<td>% of Span</td>
<td></td>
<td>5.4</td>
</tr>
</tbody>
</table>
Table 3.30 DOC interference test results.

<table>
<thead>
<tr>
<th>DOC mg/L</th>
<th>Titration Results mg/L</th>
<th>Chlorine readings from analysers (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1.15</td>
<td>0.39</td>
<td>1.33</td>
</tr>
<tr>
<td>0.94</td>
<td>0.31</td>
<td>1.08</td>
</tr>
<tr>
<td>0.73</td>
<td>0.24</td>
<td>0.83</td>
</tr>
<tr>
<td>% of Span</td>
<td>7.3</td>
<td>25.3</td>
</tr>
</tbody>
</table>

3.1.11 Summary of free chlorine analyser results

Summarised performance results for the free chlorine analysers evaluated in this study are presented in Table 3.2.

3.2 Total chlorine/monochloramine analysers

In this section, total chlorine/monochloramine analysers are labelled as follows:

- Analytical Technology, Inc. – ATi Model A 15/63
- Prominent – Dulcometer 1
- Wallace & Tiernan – Depolox 3 plus
- Applikon – Alert 2004
- Systea – MicroMac – Total Chlorine
- Systea – MicroMac – Monochloramine

3.2.1 Response, delay, rise and fall times

Table 3.31 summarises total chlorine and monochloramine analyser positive and negative response times, delay times, rise and fall times. Each result is an average result of 6 measurements.

Table 3.31 Response, delay, rise and fall times for total chlorine and monochloramine analysers.

<table>
<thead>
<tr>
<th>Analysers Characteristic (seconds)</th>
<th>Analyser Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Response time for positive change, (t_{response}), s</td>
<td>361</td>
</tr>
<tr>
<td>Delay time for positive change, (t_{delay}), s</td>
<td>57</td>
</tr>
<tr>
<td>Response time for negative change, (t_{response}), s</td>
<td>155</td>
</tr>
<tr>
<td>Delay time for negative change, (t_{delay}), s</td>
<td>52</td>
</tr>
<tr>
<td>Rise time, (t_{rise}), s</td>
<td>304</td>
</tr>
<tr>
<td>Fall time, (t_{fall}), s</td>
<td>102</td>
</tr>
</tbody>
</table>

Delay time is part of the response time (10% change) and indicates the first response of the analyser to a change in concentration. The lower this value, the faster the analyser detects changes in total chlorine concentration. Analysers 1-3 are able to measure continuously, and demonstrated faster response times to changes in sample residual concentration as compared to analysers employing a batch method of analysis (analysers 4-6). Continuously measuring analysers are preferred to batch analysers when used for process control of chemical dosing systems.
3.2.2 Linearity

Table 3.32 presents linearity test results for total chlorine and monochloramine online analysers evaluated in this study.

**Table 3.32 Total chlorine and monochloramine linearity test results**

<table>
<thead>
<tr>
<th>x_i</th>
<th>Monochloramine (mg/L)</th>
<th>Total Chlorine (mg/L)</th>
<th>Chlorine Concentration From Monitors (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>y_str</td>
<td>y_str</td>
<td>1</td>
</tr>
<tr>
<td>5%</td>
<td>0.15</td>
<td>0.21</td>
<td>0.08</td>
</tr>
<tr>
<td>20%</td>
<td>0.42</td>
<td>0.46</td>
<td>0.26</td>
</tr>
<tr>
<td>35%</td>
<td>0.69</td>
<td>0.82</td>
<td>0.54</td>
</tr>
<tr>
<td>50%</td>
<td>1.02</td>
<td>1.05</td>
<td>0.62</td>
</tr>
<tr>
<td>65%</td>
<td>1.33</td>
<td>1.38</td>
<td>1.20</td>
</tr>
<tr>
<td>80%</td>
<td>1.56</td>
<td>1.62</td>
<td>1.43</td>
</tr>
<tr>
<td>95%</td>
<td>1.91</td>
<td>2.01</td>
<td>1.92</td>
</tr>
</tbody>
</table>
Figures 3.14 to 3.19 show the results of linearity tests comparing online analyser readings (mean value of at least three measurements) plotted against laboratory analysis results.

Perfect linearity performance is when the results indicate a straight line on the hypothetical diagonal line of linearity, which means the $R^2$ value as well as the slope is equal to one. Table 3.33 presents correlation coefficient ($R^2$) and equations for the individual total chlorine analysers evaluated in this study over the sample concentration range.
Table 3.33 Equation of linearity and correlation coefficient for total chlorine/monochloramine analysers.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
<td>0.8549x</td>
<td>0.8661x</td>
<td>1.0621x</td>
<td>0.9580x</td>
<td>1.0605x</td>
<td>1.0262x</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9335</td>
<td>0.9064</td>
<td>0.9907</td>
<td>0.9973</td>
<td>0.9262</td>
<td>0.9518</td>
</tr>
</tbody>
</table>

3.2.3 Coefficient of variation

Table 3.34 presents coefficient of variance results (COV) for the total chlorine and monochloramine analysers evaluated in this study. The experimental data that was used to calculate the COVs was the same as that used for linearity tests. The COV is zero if the results produced by an analyser match exactly the titrations or reference results. The more the analyser drifts, the bigger the COV.

Table 3.34 COV for total chlorine/monochloramine analysers

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>COV, %</td>
<td>28</td>
<td>32</td>
<td>11</td>
<td>7</td>
<td>21</td>
<td>16</td>
</tr>
</tbody>
</table>

3.2.4 Limit of detection and limit of quantification

Table 3.35 shows total chlorine and monochloramine online analyser limit of detection and limit of quantification results.

Table 3.35 Standard deviations and LOD for total chlorine/monochloramine analysers

<table>
<thead>
<tr>
<th></th>
<th>STD, mg/L</th>
<th>LOD, mg/L</th>
<th>LOQ, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration mg/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.16</td>
<td>0.14</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>Titration Total Chlorine mg/L</td>
<td>0.21</td>
<td>0.20</td>
<td>0.21</td>
</tr>
<tr>
<td>Monitor - 1 mg/L</td>
<td>0.09</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>Monitor - 2 mg/L</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Monitor - 3 mg/L</td>
<td>0.17</td>
<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td>Monitor - 4 mg/L</td>
<td>0.18</td>
<td>0.23</td>
<td>0.15</td>
</tr>
<tr>
<td>Monitor - 5 mg/L</td>
<td>0.14</td>
<td>0.18</td>
<td>0.21</td>
</tr>
<tr>
<td>Monitor - 6 mg/L</td>
<td>0.26</td>
<td>0.26</td>
<td>0.41</td>
</tr>
</tbody>
</table>

3.2.5 Repeatability and day-to-day repeatability

Tables 3.36 and 3.37 present repeatability results for monochloramine and total chlorine at 20% and 80% of the measuring range respectively.
Table 3.36 Repeatability results at 20% of the measuring range for total chlorine/monochloramine analysers

<table>
<thead>
<tr>
<th>No. of measurement</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>RPT 20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration (Mono. Cl) mg/L</td>
<td>0.44</td>
<td>0.44</td>
<td>0.43</td>
<td>0.42</td>
<td>0.41</td>
<td>0.40</td>
<td>0.02</td>
</tr>
<tr>
<td>Titration (Total Cl) mg/L</td>
<td>0.48</td>
<td>0.47</td>
<td>0.48</td>
<td>0.46</td>
<td>0.46</td>
<td>0.44</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 1 mg/L</td>
<td>0.28</td>
<td>0.30</td>
<td>0.27</td>
<td>0.24</td>
<td>0.23</td>
<td>0.23</td>
<td>0.03</td>
</tr>
<tr>
<td>Analyser - 2 mg/L</td>
<td>0.43</td>
<td>0.45</td>
<td>0.45</td>
<td>0.43</td>
<td>0.43</td>
<td>0.44</td>
<td>0.01</td>
</tr>
<tr>
<td>Analyser - 3 mg/L</td>
<td>0.52</td>
<td>0.50</td>
<td>0.49</td>
<td>0.48</td>
<td>0.47</td>
<td>0.45</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 4 mg/L</td>
<td>0.41</td>
<td>0.42</td>
<td>0.44</td>
<td>0.43</td>
<td>0.40</td>
<td>0.43</td>
<td>0.01</td>
</tr>
<tr>
<td>Analyser - 5 mg/L</td>
<td>0.31</td>
<td>0.31</td>
<td>0.46</td>
<td>0.49</td>
<td>0.48</td>
<td>0.48</td>
<td>0.09</td>
</tr>
<tr>
<td>Analyser - 6 mg/L</td>
<td>0.51</td>
<td>0.51</td>
<td>0.56</td>
<td>0.61</td>
<td>0.61</td>
<td>0.77</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 3.37 Repeatability results at 80% of the measuring range for total chlorine/monochloramine analysers.

<table>
<thead>
<tr>
<th>No. of measurement</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>RPT 80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration (Mono. Cl) mg/L</td>
<td>1.58</td>
<td>1.59</td>
<td>1.57</td>
<td>1.56</td>
<td>1.53</td>
<td>1.51</td>
<td>0.03</td>
</tr>
<tr>
<td>Titration (Total Cl) mg/L</td>
<td>1.63</td>
<td>1.65</td>
<td>1.63</td>
<td>1.63</td>
<td>1.60</td>
<td>1.57</td>
<td>0.03</td>
</tr>
<tr>
<td>Analyser - 1 mg/L</td>
<td>1.19</td>
<td>1.29</td>
<td>1.32</td>
<td>1.37</td>
<td>1.40</td>
<td>1.43</td>
<td>0.09</td>
</tr>
<tr>
<td>Analyser - 2 mg/L</td>
<td>1.93</td>
<td>1.89</td>
<td>1.84</td>
<td>1.80</td>
<td>1.72</td>
<td>1.71</td>
<td>0.09</td>
</tr>
<tr>
<td>Analyser - 3 mg/L</td>
<td>1.74</td>
<td>1.75</td>
<td>1.74</td>
<td>1.72</td>
<td>1.70</td>
<td>1.69</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 4 mg/L</td>
<td>1.63</td>
<td>1.63</td>
<td>1.60</td>
<td>1.63</td>
<td>1.53</td>
<td>1.64</td>
<td>0.04</td>
</tr>
<tr>
<td>Analyser - 5 mg/L</td>
<td>0.12</td>
<td>0.12</td>
<td>1.48</td>
<td>1.61</td>
<td>1.64</td>
<td>0.33</td>
<td>0.09</td>
</tr>
<tr>
<td>Analyser - 6 mg/L</td>
<td>0.26</td>
<td>1.33</td>
<td>1.74</td>
<td>1.74</td>
<td>1.74</td>
<td>1.74</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Day-to-day repeatability data was collected over a six-day period using a 35% and 65% test solution and results are presented in tables 38 and 39 respectively. Each data point represents a daily adjusted concentration and is the mean value of at least three measurements after the analyser was stable in its reading.
Table 3.38 Day-to-day repeatability results at 35% of the measuring range for total chlorine/monochloramine analysers

<table>
<thead>
<tr>
<th>Day Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>RPT 35%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration (Mono. Cl) mg/L</td>
<td>0.65</td>
<td>0.69</td>
<td>0.73</td>
<td>0.73</td>
<td>0.72</td>
<td>0.74</td>
<td>0.03</td>
</tr>
<tr>
<td>Titration (Total Cl) mg/L</td>
<td>0.75</td>
<td>0.82</td>
<td>0.77</td>
<td>0.79</td>
<td>0.77</td>
<td>0.78</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 1 mg/L</td>
<td>0.32</td>
<td>0.54</td>
<td>0.25</td>
<td>0.28</td>
<td>0.25</td>
<td>0.33</td>
<td>0.11</td>
</tr>
<tr>
<td>Analyser - 2 mg/L</td>
<td>0.82</td>
<td>0.80</td>
<td>0.58</td>
<td>0.83</td>
<td>0.45</td>
<td>0.55</td>
<td>0.16</td>
</tr>
<tr>
<td>Analyser - 3 mg/L</td>
<td>0.81</td>
<td>0.87</td>
<td>0.92</td>
<td>0.87</td>
<td>0.85</td>
<td>0.83</td>
<td>0.04</td>
</tr>
<tr>
<td>Analyser - 4 mg/L</td>
<td>-</td>
<td>0.73</td>
<td>0.75</td>
<td>0.75</td>
<td>0.70</td>
<td>0.74</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser - 5 mg/L</td>
<td>0.16</td>
<td>0.79</td>
<td>0.70</td>
<td>0.77</td>
<td>0.66</td>
<td>0.67</td>
<td>0.06</td>
</tr>
<tr>
<td>Analyser - 6 mg/L</td>
<td>0.51</td>
<td>0.71</td>
<td>0.77</td>
<td>0.77</td>
<td>0.66</td>
<td>0.82</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Table 3.39 Results for day-to-day repeatability at 65% of the measuring range

<table>
<thead>
<tr>
<th>Day number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>RPT 65%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration (Mono. Cl) mg/L</td>
<td>1.31</td>
<td>1.28</td>
<td>1.32</td>
<td>1.29</td>
<td>1.33</td>
<td>1.27</td>
<td>0.02</td>
</tr>
<tr>
<td>Titration (Total Cl) mg/L</td>
<td>1.39</td>
<td>1.32</td>
<td>1.38</td>
<td>1.35</td>
<td>1.38</td>
<td>1.32</td>
<td>0.03</td>
</tr>
<tr>
<td>Analyser - 1 mg/L</td>
<td>1.12</td>
<td>1.04</td>
<td>1.00</td>
<td>0.81</td>
<td>1.20</td>
<td>1.79</td>
<td>0.34</td>
</tr>
<tr>
<td>Analyser - 2 mg/L</td>
<td>1.13</td>
<td>1.08</td>
<td>1.29</td>
<td>2.19</td>
<td>0.93</td>
<td>1.36</td>
<td>0.45</td>
</tr>
<tr>
<td>Analyser - 3 mg/L</td>
<td>1.60</td>
<td>1.51</td>
<td>1.51</td>
<td>1.50</td>
<td>1.48</td>
<td>1.21</td>
<td>0.13</td>
</tr>
<tr>
<td>Analyser - 4 mg/L</td>
<td>0.99</td>
<td>1.32</td>
<td>1.29</td>
<td>1.35</td>
<td>1.30</td>
<td>1.26</td>
<td>0.13</td>
</tr>
<tr>
<td>Analyser - 5 mg/L</td>
<td>1.43</td>
<td>1.25</td>
<td>1.35</td>
<td>1.34</td>
<td>1.31</td>
<td>1.92</td>
<td>0.25</td>
</tr>
<tr>
<td>Analyser - 6 mg/L</td>
<td>1.38</td>
<td>1.28</td>
<td>1.07</td>
<td>1.17</td>
<td>1.23</td>
<td>1.07</td>
<td>0.12</td>
</tr>
</tbody>
</table>

3.2.6 Lowest detectable change

Lowest detectable change (LDC) was calculated using the same data that was used to calculate repeatability performance indicators. LDC is defined as three times the standard derivation. Tables 3.40 and 3.41 present LDC results determined at concentrations equivalent to 20% and 80% of the working range. Analysers having a small LDC have the ability to detect small changes in concentration and analysers having a high LDC are not able to detect small changes in concentration. Ideally the LDC for an online analyser should be as close as possible to the LDC of the titration. It should be noted that the concentration of monochloramine in the sample recirculating in the test rig was not completely stable during the trial. The LDC of the titrations was 0.05 mg/L for the 20% test solution and 0.09 mg/L for the 80% test solution. An analyser having ideal LDC performance would achieve identical LDC values for the 20% (0.05 mg/L) and for the 80% solution (0.09 mg/L).
**Table 3.40** Results for LDC at 20% of the measuring range

<table>
<thead>
<tr>
<th>No. of measurement</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>STD, mg/L</th>
<th>LDC, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration (Mono. Cl)</td>
<td>0.44</td>
<td>0.44</td>
<td>0.43</td>
<td>0.42</td>
<td>0.41</td>
<td>0.40</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Titration (Total Cl)</td>
<td>0.48</td>
<td>0.47</td>
<td>0.48</td>
<td>0.46</td>
<td>0.46</td>
<td>0.44</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Analyser - 1</td>
<td>0.28</td>
<td>0.30</td>
<td>0.27</td>
<td>0.24</td>
<td>0.23</td>
<td>0.23</td>
<td>0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>0.43</td>
<td>0.45</td>
<td>0.45</td>
<td>0.43</td>
<td>0.43</td>
<td>0.44</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>0.52</td>
<td>0.50</td>
<td>0.49</td>
<td>0.48</td>
<td>0.47</td>
<td>0.45</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>0.41</td>
<td>0.42</td>
<td>0.44</td>
<td>0.43</td>
<td>0.40</td>
<td>0.43</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>0.31</td>
<td>0.31</td>
<td>0.46</td>
<td>0.49</td>
<td>0.48</td>
<td>0.48</td>
<td>0.09</td>
<td>0.26</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>0.51</td>
<td>0.51</td>
<td>0.56</td>
<td>0.61</td>
<td>0.61</td>
<td>0.77</td>
<td>0.10</td>
<td>0.29</td>
</tr>
</tbody>
</table>

**Table 3.41** Results for LDC at 80% of the measuring range.

<table>
<thead>
<tr>
<th>No. of measurement</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>STD, mg/L</th>
<th>LDC, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration (Mono. Cl)</td>
<td>1.58</td>
<td>1.59</td>
<td>1.57</td>
<td>1.56</td>
<td>1.53</td>
<td>1.51</td>
<td>0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>Titration (Total Cl)</td>
<td>1.63</td>
<td>1.65</td>
<td>1.63</td>
<td>1.63</td>
<td>1.60</td>
<td>1.57</td>
<td>0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>Analyser - 1</td>
<td>1.19</td>
<td>1.29</td>
<td>1.32</td>
<td>1.37</td>
<td>1.40</td>
<td>1.43</td>
<td>0.09</td>
<td>0.26</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>1.93</td>
<td>1.89</td>
<td>1.84</td>
<td>1.80</td>
<td>1.72</td>
<td>1.71</td>
<td>0.09</td>
<td>0.27</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>1.74</td>
<td>1.75</td>
<td>1.74</td>
<td>1.72</td>
<td>1.70</td>
<td>1.69</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>1.63</td>
<td>1.63</td>
<td>1.60</td>
<td>1.63</td>
<td>1.53</td>
<td>1.64</td>
<td>0.04</td>
<td>0.12</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>-</td>
<td>-</td>
<td>1.48</td>
<td>1.61</td>
<td>1.64</td>
<td>-</td>
<td>0.09</td>
<td>0.26</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>-</td>
<td>-</td>
<td>1.74</td>
<td>1.74</td>
<td>1.74</td>
<td>1.74</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
3.2.7 Bias

Bias is an indicator of any systematic measuring errors exhibited by an online analyser. The data used to calculate bias was the same as that used to determine repeatability and LDC. The laboratory analysis results did not have any impact on the calculated repeatability and LDC value; it was only used to control the concentration of the test solution. Analysers can perform well in terms of repeatability and LDC but they can be biased and the analyser reading can be different to the actual concentration. Tables 3.42 and 3.43 present bias results for online total chlorine/monochloramine analysers using 20% and 80% test solutions.

**Table 3.42** Results for bias at 20% of the measuring range.

<table>
<thead>
<tr>
<th>No. of measurement</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Mean, mg/L</th>
<th>Bias, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration (Mono. Cl)</td>
<td>mg/L</td>
<td>0.44</td>
<td>0.44</td>
<td>0.43</td>
<td>0.42</td>
<td>0.41</td>
<td>0.40</td>
<td>0.42</td>
</tr>
<tr>
<td>Titration (Total Cl)</td>
<td>mg/L</td>
<td>0.48</td>
<td>0.47</td>
<td>0.48</td>
<td>0.46</td>
<td>0.46</td>
<td>0.44</td>
<td>0.47</td>
</tr>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>0.28</td>
<td>0.30</td>
<td>0.27</td>
<td>0.24</td>
<td>0.23</td>
<td>0.23</td>
<td>0.26</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>0.43</td>
<td>0.45</td>
<td>0.45</td>
<td>0.43</td>
<td>0.43</td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>0.52</td>
<td>0.50</td>
<td>0.49</td>
<td>0.48</td>
<td>0.47</td>
<td>0.45</td>
<td>0.49</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>0.41</td>
<td>0.42</td>
<td>0.44</td>
<td>0.43</td>
<td>0.40</td>
<td>0.43</td>
<td>0.42</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>0.31</td>
<td>0.31</td>
<td>0.46</td>
<td>0.49</td>
<td>0.48</td>
<td>0.48</td>
<td>0.42</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>0.51</td>
<td>0.51</td>
<td>0.56</td>
<td>0.61</td>
<td>0.61</td>
<td>0.77</td>
<td>0.60</td>
</tr>
</tbody>
</table>

**Table 3.43** Results for bias at 80% of the measuring range.

<table>
<thead>
<tr>
<th>No. of measurement</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Mean, mg/L</th>
<th>Bias, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titration (Mono. Cl)</td>
<td>mg/L</td>
<td>1.58</td>
<td>1.59</td>
<td>1.57</td>
<td>1.56</td>
<td>1.53</td>
<td>1.51</td>
<td>1.56</td>
</tr>
<tr>
<td>Titration (Total Cl)</td>
<td>mg/L</td>
<td>1.63</td>
<td>1.65</td>
<td>1.63</td>
<td>1.63</td>
<td>1.60</td>
<td>1.57</td>
<td>1.62</td>
</tr>
<tr>
<td>Analyser - 1</td>
<td>mg/L</td>
<td>1.19</td>
<td>1.29</td>
<td>1.32</td>
<td>1.37</td>
<td>1.40</td>
<td>1.43</td>
<td>1.33</td>
</tr>
<tr>
<td>Analyser - 2</td>
<td>mg/L</td>
<td>1.93</td>
<td>1.89</td>
<td>1.84</td>
<td>1.80</td>
<td>1.72</td>
<td>1.71</td>
<td>1.82</td>
</tr>
<tr>
<td>Analyser - 3</td>
<td>mg/L</td>
<td>1.74</td>
<td>1.75</td>
<td>1.74</td>
<td>1.72</td>
<td>1.70</td>
<td>1.69</td>
<td>1.72</td>
</tr>
<tr>
<td>Analyser - 4</td>
<td>mg/L</td>
<td>1.63</td>
<td>1.63</td>
<td>1.60</td>
<td>1.63</td>
<td>1.53</td>
<td>1.64</td>
<td>1.61</td>
</tr>
<tr>
<td>Analyser - 5</td>
<td>mg/L</td>
<td>-</td>
<td>-</td>
<td>1.48</td>
<td>1.61</td>
<td>1.64</td>
<td>-</td>
<td>0.09</td>
</tr>
<tr>
<td>Analyser - 6</td>
<td>mg/L</td>
<td>-</td>
<td>-</td>
<td>1.74</td>
<td>1.74</td>
<td>1.74</td>
<td>1.74</td>
<td>0.00</td>
</tr>
</tbody>
</table>

A bias effect can be reduced by recalibrating an analyser, and is not related to the accuracy of an analyser.
3.2.8 Short-term drift

Table 3.44 presents summarised results for short term drift (ShTD) for online total chlorine and monochloramine analysers determined using an 80% test solution. The ISO standard recommends a 50% solution to be used, however, the measuring period during the experiment was too short using the 50% solution to calculate the ShTD. The ShTD was detected over a period of 85 minutes. Analysers 4 to 6 employ a batch-wise operation and supply fewer data points to properly determine the regression as compared to the continuous measuring analysers (analysers 1 to 3).

<table>
<thead>
<tr>
<th>Titration (Mono. Cl.)</th>
<th>mg/L</th>
<th>Slope, (mg/L)/hour</th>
<th>ShTD, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0594</td>
<td>-2.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0514</td>
<td>-2.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1554</td>
<td>7.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1782</td>
<td>-8.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0627</td>
<td>-3.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0193</td>
<td>-0.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1611</td>
<td>8.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2184</td>
<td>10.92</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2.9 Memory effects

Analysers were calibrated and then subjected to a memory effect test. Analysers were first exposed to a concentration equivalent to 200% of the working range and then to the 20% (0.4 mg/L) test solution. Results at the 20% solution were logged and compared to results obtained using laboratory analysis. Each result represents an average of at least three readings obtained from the analysers. Table 3.45 presents results from the memory effect test.

An analyser performs well if the reading falls on a straight line and stays close to or follows the titration line. The calculated values shown in Table 3.46 are the mean values of the analyser readings subtracted from the mean values of the titrations (total chlorine and monochloramine values are used for analysers 1 to 5 and 6 respectively).

<table>
<thead>
<tr>
<th>No.</th>
<th>Titrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mono</td>
</tr>
<tr>
<td>1</td>
<td>y\text{titr}</td>
</tr>
<tr>
<td>2</td>
<td>y\text{titr}</td>
</tr>
<tr>
<td>3</td>
<td>y\text{titr}</td>
</tr>
<tr>
<td>4</td>
<td>y\text{titr}</td>
</tr>
<tr>
<td>5</td>
<td>y\text{titr}</td>
</tr>
<tr>
<td>6</td>
<td>y\text{titr}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Readings from Analysers [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mono</td>
</tr>
<tr>
<td>1</td>
<td>y_{i,1}</td>
</tr>
<tr>
<td>2</td>
<td>y_{i,3}</td>
</tr>
<tr>
<td>3</td>
<td>y_{i,5}</td>
</tr>
<tr>
<td>4</td>
<td>y_{i,7}</td>
</tr>
<tr>
<td>5</td>
<td>y_{i,9}</td>
</tr>
<tr>
<td>6</td>
<td>y_{i,11}</td>
</tr>
</tbody>
</table>

Table 3.45 Results at 20% of the measuring range for memory effect tests

<table>
<thead>
<tr>
<th>No.</th>
<th>Titrations</th>
<th>Readings from Analysers [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mono</td>
<td>Tot. Cl.</td>
</tr>
<tr>
<td>1</td>
<td>0.34</td>
<td>0.39</td>
</tr>
<tr>
<td>2</td>
<td>0.43</td>
<td>0.46</td>
</tr>
<tr>
<td>3</td>
<td>0.38</td>
<td>0.42</td>
</tr>
<tr>
<td>4</td>
<td>0.39</td>
<td>0.42</td>
</tr>
<tr>
<td>5</td>
<td>0.38</td>
<td>0.41</td>
</tr>
<tr>
<td>6</td>
<td>0.41</td>
<td>0.45</td>
</tr>
<tr>
<td>Average:</td>
<td>0.39</td>
<td>0.43</td>
</tr>
</tbody>
</table>
Table 3.46 Memory effect results for total chlorine/monochloramine analysers.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of measuring range, [2 mg/L]</td>
<td>44</td>
<td>57</td>
<td>42</td>
<td>6</td>
<td>15</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2.10 pH Dependence.

Figure 3.20 displays the output from total chlorine analysers evaluated in this study in response to a range in sample total chlorine concentration (1.3 – 1.9 mg/L) at a range in sample pH (5-10). The closer the analyser readings are to the reference measurement result (diagonal line), the better the performance of the analyser.

Sample pH was increased in 4 steps (pH 5 to 10) and can be seen by the solid line. The black thin line starting at value 1 on the x-axis and the primary y-axis is the hypothetical diagonal line. The closer the analyser readings are to the diagonal line, the more accurate and better are their results.

Table 3.47 Results of pH dependence for total chlorine/monochloramine analysers.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of measuring range, [2 mg/L]</td>
<td>44</td>
<td>57</td>
<td>42</td>
<td>6</td>
<td>15</td>
<td>-</td>
</tr>
</tbody>
</table>
3.2.11 Conductivity dependence

In this study, the electrolytic conductivity of the sample was changed in three steps from 250 µS/cm (low conductivity) then to 500 µS/cm (moderate conductivity) and finally to 880 µS/cm (high conductivity). The water used during all other tests had a conductivity of approximately 550 µS/cm. The low conductivity water was prepared by adding distilled water to the test solution. The moderate and high conductivity water samples were prepared by adding potassium chloride. The response of the total chlorine/monochloramine online analysers to changes in sample total chlorine/monochloramine concentration at various conductivities is shown in Figure 3.21. Each measurement is the average of at least three measurements made by the analyser. The primary y-axis shows the measured concentration and the secondary y-axis the conductivity of the sample. The monochloramine and total chlorine concentration during this trial ranged from 1.0 to 1.2 mg/L and was confirmed by laboratory analysis.

Figure 3.21 Impact of conductivity on total chlorine/monochloramine analysers.

Table 3.48 shows the calculated results for this trial. The results are calculated in a similar way to the method used for pH dependence. All values are in the range of the results of the repeatability, as shown previously. Analyser 6 showed also strong variation in the repeatability results which means the conductivity change was not responsible for the variation in the measurements.

Table 3.48 Impact of conductivity on total chlorine/monochloramine analysers.

<table>
<thead>
<tr>
<th>Analyser number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of measuring range, [2 mg/L]</td>
<td>0.9</td>
<td>2.0</td>
<td>1.5</td>
<td>1.0</td>
<td>3.5</td>
<td>12.4</td>
</tr>
</tbody>
</table>

3.2.12 Summary of total chlorine/monochloramine analyser results

Summarised performance results for the five total chlorine and one monochloramine analyser evaluated in this study are presented in Table 3.3.
3.3 Ammonia trial results

This section contains the result and discussion for three ammonia analysers that were evaluated in this trial. Ammonia analysers are labelled as follows:

- Applikon - ADI 2018
- Endress & Hauser – StamoLys CA 71 AM
- SYSTEAM – MicroMac – Ammonia

Analyser 1 uses an ammonia selective electrode method and delivers readings as free ammonia, analysers 2 and 3 measure total ammonia concentrations with a colorimetric system using a phenate based method. Results from online analysers were compared to results obtained from a commercial hand held colorimetric analyser (Hach DR 890, Hach, Loveland Co, USA) that employed a phenate method. This provided reference data which was used to calculate some of the analyser performance characteristics.

3.3.1 Response times

All ammonia analysers investigated in this study are discontinuous and measure ammonia in a batch mode prohibiting the determination of delay, rise and fall times. The response times for negative and positive change are in shown Table 49. The discontinuous mode of measurement employed by all ammonia analysers evaluated gives rise to relatively long response times as compared to continuous analysers previously investigated.

Table 3.49 Average response times for ammonia analysers.

<table>
<thead>
<tr>
<th>Analyser Characteristic</th>
<th>Analyser Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Response time for positive change, (t_response_+), s</td>
<td>1370</td>
</tr>
<tr>
<td>Delay time for positive change, (t_delay_+), s</td>
<td>-</td>
</tr>
<tr>
<td>Response time for negative change, (t_response_-), s</td>
<td>1452</td>
</tr>
<tr>
<td>Delay time for negative change, (t_delay_-), s</td>
<td>-</td>
</tr>
<tr>
<td>Rise time, (t_rise), s</td>
<td>-</td>
</tr>
<tr>
<td>Fall time, (t_fall), s</td>
<td>-</td>
</tr>
</tbody>
</table>

3.3.2 Linearity

Ammonia analyser linearity performance is presented in Figures 3.22 to 3.24. Results from this study show that all analysers possess good linearity (R\(^2\) values >0.98) but exhibit variable regression line slopes (Table 3.50).
Analyser 1 is factory calibrated and performed an automatic calibration during trials, however only for the zero offset. This is the only ammonia that does not use a colorimetric method and as the reference analyser (Hach DR 890) employs a colorimetric technique, differences between the two may be as a result of a systematic error.

Table 3.50 Ammonia analyser equation for linearity and correlation coefficient

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
<td>1.3297x</td>
<td>1.1537x</td>
<td>1.1273x</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9962</td>
<td>0.9931</td>
<td>0.9847</td>
</tr>
</tbody>
</table>
3.3.3 Coefficient of variation
The calculation of the COV is based on the data for linearity and is presented in Table 3.51.

Table 3.51 COV for ammonia analysers

<table>
<thead>
<tr>
<th></th>
<th>Analyser</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>COV, %</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>34.2</td>
<td>18.9</td>
<td>17.7</td>
</tr>
</tbody>
</table>

3.3.4 Limit of detection and limit of quantification
Limit of detection was determined using a 5% test solution that had an ammonia concentration of 0.05 mg/L as NH$_3$-N and are presented in Table 3.52. Analysers 1 and 2 were able to detect ammonia at a lower concentration than analyser 3 (0.02 mg/L as compared to 0.07 mg/L). Table 3.52 also presents limit of quantification results for the ammonia analysers evaluated in this study. It can be seen that analysers 1 and 2 show similar results with an LOQ equivalent to 0.05 mg/L. This concentration is the lowest ammonia concentration, which can be detected with a level of precision and accuracy and is similar to the LOQ obtained for chlorine analysers. Analyser 3 could not be used to measure concentrations below 0.23 mg/L precisely.

Table 3.52 Standard deviation and LOD results for ammonia analysers.

<table>
<thead>
<tr>
<th>Ammonia HACH DR 890</th>
<th>STD</th>
<th>LOD</th>
<th>LOQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/L of NH$_3$-N</td>
<td>0.007</td>
<td>0.020</td>
<td>0.066</td>
</tr>
<tr>
<td>Analyser 1</td>
<td>mg/L</td>
<td>0.005</td>
<td>0.016</td>
</tr>
<tr>
<td>Analyser 2</td>
<td>mg/L</td>
<td>0.005</td>
<td>0.015</td>
</tr>
<tr>
<td>Analyser 3</td>
<td>mg/L</td>
<td>0.023</td>
<td>0.070</td>
</tr>
</tbody>
</table>

3.3.5 Repeatability
Repeatability performance for 20 and 80% test solution are presented in Figures 3.25 and 3.26 respectively. Table 3.53 presents the calculated results for repeatability which is equal to the standard derivation of the measured results.

Figure 3.25 Repeatability of ammonia analysers for 20% of the working range.
Figure 3.26 Repeatability of ammonia analysers for 80% of measuring range.

Table 3.53 Repeatability results for ammonia analysers at 20 and 80% of the measuring range.

<table>
<thead>
<tr>
<th>Test solution conc., % of the range</th>
<th>20</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>STD</td>
<td>STD</td>
</tr>
<tr>
<td>Ammonia HACH DR 890 mg/L of NH₃-N</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser 1</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser 2</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>Analyser 3</td>
<td>0.02</td>
<td>0.10</td>
</tr>
</tbody>
</table>

3.3.6 Day-to-day repeatability

Results for the day-to-day repeatability at 35 and 65% of the working range are shown in Figures 3.27 and 3.28 respectively and Table 3.54 gives results for both concentrations.
Figure 3.27 Day-to-day repeatability data for ammonia analysers at 35% of the measuring range.

Figure 3.28 Day-to-day repeatability data for ammonia analysers for 65% of the measuring range.

Table 3.54 Day-to-day repeatability results for ammonia analysers at 35 and 65% of the measuring range.

<table>
<thead>
<tr>
<th>Test solution conc., % of the range</th>
<th>35</th>
<th>65</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>STD</td>
<td>STD</td>
</tr>
<tr>
<td>Ammonia HACH DR 890</td>
<td>mg/L of NH₃-N</td>
<td>0.01</td>
</tr>
<tr>
<td>Analyser 1</td>
<td>mg/L</td>
<td>0.05</td>
</tr>
<tr>
<td>Analyser 2</td>
<td>mg/L</td>
<td>0.02</td>
</tr>
<tr>
<td>Analyser 3</td>
<td>mg/L</td>
<td>0.02</td>
</tr>
</tbody>
</table>
3.3.7 Lowest detectable change

Lowest detectable change is calculated for a 20% and 80% test solution using the same data that was used for repeatability calculations (see Table 3.55). The LDC is calculated as three times the standard deviation of the measurements similar to the calculation of LOD. These values increase with the concentration of the test solution.

Table 3.55 LDC results for ammonia analysers at 20 and 80% of the measuring range.

<table>
<thead>
<tr>
<th>Test solution conc., % of the range</th>
<th align="right">20</th>
<th align="right">80</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td align="right">STD</td>
<td align="right">LDC</td>
</tr>
<tr>
<td>Ammonia HACH DR 890 mg/L of NH₃-N</td>
<td align="right">0.00</td>
<td align="right">0.01</td>
</tr>
<tr>
<td>Analyser 1 mg/L</td>
<td align="right">0.02</td>
<td align="right">0.05</td>
</tr>
<tr>
<td>Analyser 2 mg/L</td>
<td align="right">0.00</td>
<td align="right">0.01</td>
</tr>
<tr>
<td>Analyser 3 mg/L</td>
<td align="right">0.02</td>
<td align="right">0.07</td>
</tr>
</tbody>
</table>

3.3.8 Bias

As can be seen in graphs showing linearity and repeatability trends, all ammonia analysers showed a trend to drift on higher concentrations. Referred to bias, this can be seen in results presented in Tables 3.56 and 3.57.

Table 3.56 Bias for ammonia analysers at 20% of the measuring range.

<table>
<thead>
<tr>
<th>No. of measurement</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Mean</th>
<th>Bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia HACH DR 890</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mg/L of NH₃-N</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
<td>0.22</td>
<td>0.21</td>
<td>-</td>
</tr>
<tr>
<td>Analyser - 1 mg/L</td>
<td>0.20</td>
<td>0.24</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.24</td>
<td>0.24</td>
<td>0.03</td>
</tr>
<tr>
<td>Analyser - 2 mg/L</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
<td>0.21</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
<td>0.01</td>
</tr>
<tr>
<td>Analyser - 3 mg/L</td>
<td>0.21</td>
<td>0.24</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.26</td>
<td>0.25</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 3.57 Bias for ammonia analysers at 80% of the measuring range.

<table>
<thead>
<tr>
<th>No. of measurement</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Mean</th>
<th>Bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia HACH DR 890</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mg/L of NH3-N</td>
<td>0.82</td>
<td>0.81</td>
<td>0.79</td>
<td>0.76</td>
<td>0.77</td>
<td>0.79</td>
<td>0.79</td>
<td>-</td>
</tr>
<tr>
<td>Analyser - 1 mg/L</td>
<td>1.02</td>
<td>1.08</td>
<td>1.08</td>
<td>1.06</td>
<td>1.08</td>
<td>1.07</td>
<td>1.06</td>
<td>0.27</td>
</tr>
<tr>
<td>Analyser - 2 mg/L</td>
<td>0.94</td>
<td>0.94</td>
<td>0.95</td>
<td>0.97</td>
<td>0.96</td>
<td>0.95</td>
<td>0.95</td>
<td>0.16</td>
</tr>
<tr>
<td>Analyser - 3 mg/L</td>
<td>0.73</td>
<td>0.85</td>
<td>0.93</td>
<td>0.96</td>
<td>0.98</td>
<td>0.98</td>
<td>0.91</td>
<td>0.12</td>
</tr>
</tbody>
</table>
3.3.9 Short-Term Drift

Figure 3.29 presents data that was used to determine short term drift using an 80% test solution. Short term drift results are presented in Table 3.58. It should be remembered that all ammonia analysers are discontinuous and operate in a batch mode. This reduces the number of results that can be used to determine the short term drift.

![Graph showing short-term drift data for ammonia analysers](image)

**Table 3.58** Short-term drift results for ammonia analysers

<table>
<thead>
<tr>
<th>Ammonia HACH DR 890</th>
<th>Slope, (mg/L)hour</th>
<th>ShTD, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/L of NH₃-N</td>
<td>-0.0343</td>
<td>-1.15</td>
</tr>
<tr>
<td>Analyser 1</td>
<td>0.0229</td>
<td>2.29</td>
</tr>
<tr>
<td>mg/L</td>
<td>0.0000</td>
<td>0.00</td>
</tr>
<tr>
<td>Analyser 2</td>
<td>0.0903</td>
<td>9.03</td>
</tr>
<tr>
<td>mg/L</td>
<td>-0.0000</td>
<td>0.00</td>
</tr>
<tr>
<td>Analyser 3</td>
<td>-0.0000</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Figure 3.29** Short-term drift data for ammonia analysers
3.3.10 Memory Effect

Figure 3.30 and Table 3.59 show results for memory tests. All values are in the range of the bias effect, and cannot be related to a memory effect.

![Figure 3.30 Memory effect data for ammonia analysers](image)

Table 3.59 Memory effect results for ammonia analysers

<table>
<thead>
<tr>
<th></th>
<th>Analyser 1</th>
<th>Analyser 2</th>
<th>Analyser 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowest detectable change at 20% of the measuring range, mg/L</td>
<td>0.05</td>
<td>0.01</td>
<td>0.07</td>
</tr>
<tr>
<td>Difference between mean analyser and laboratory test readings, mg/L</td>
<td>0.07</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>Memory Effect for Analysers, (Yes/No)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

3.3.11 Interferences

Results showing the response of ammonia analysers to variation in water quality (pH, conductivity and chlorine:ammonia ratio) are presented when subjected to an ammonia concentration of 0.5mg/L (50% test solution).

pH Dependence

Figure 3.31 shows results of the pH dependence test for the ammonia analysers. The primary y-axis shows ammonia concentrations, which is approximately 0.5 mg/L (+/- 0.06 mg/L). The black solid line follows the pH changes which are plotted on the secondary y-axis. All analysers show a linear decreasing trend.
Figure 3.31 pH interference data for ammonia analysers

Table 3.60 shows calculated results as a percentage of the 1 mg/L working range. It can be seen that results for all analysers are less than the value obtained for the reference measurement (Hach DR 890) indicating minimal pH interference.

Table 3.60 pH interference results for ammonia analysers

<table>
<thead>
<tr>
<th>% of the working range, [1 mg/L]</th>
<th>HACH DR 890</th>
<th>Analyser 1</th>
<th>Analyser 2</th>
<th>Analyser 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.5</td>
<td>3.7</td>
<td>6.0</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Conductivity

Figure 3.32 shows the impact of electrolytic on ammonia analyser performance. The conductivity test was undertaken in a similar way to the pH test and the solid black line shows changes in conductivity. Results indicate that conductivity in the range 250 to 850 µS/cm has minimal impact on ammonia analysers’ performance.

The calculated values presented in Table 3.61 confirm the trends shown in Figure 3.32 and show that the ammonia analysers exhibit an equal or smaller variation in percent of the working range as compared to the reference instrument.
Figure 3.32 Conductivity interference data for ammonia analysers

Table 3.61 Conductivity interference results for ammonia analysers

<table>
<thead>
<tr>
<th>% of the working range, [1 mg/L]</th>
<th>Analyser 1</th>
<th>Analyser 2</th>
<th>Analyser 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.0</td>
<td>2.0</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Variation of chlorine-to-ammonia ratios

The ideal chlorine-to-ammonia ratio is 4.5:1 for chloramination of potable supplies however conditions in the WDS may lead to non ideal ratios being formed (AWWARF 2004). The following section presents the performance of ammonia analysers to ideal and non ideal ratios.

Ideal chlorine-to-ammonia ratio

Figure 3.33 shows the ammonia analyser performance when subjected to the ideal chlorine to ammonia ratio (4.5:1) for a chloraminated water supply.

The analysers were exposed to an ammonia concentration of 0.5 mg/L at the start of the trial (time 0). The analyser readings were stabilised after approximately 40 minutes. At this point chlorine stock solution was dosed to the tank and mixed to form monochloramine. No impact was shown by analysers 2, 3 or the reference measurement (Hach DR890). These analysers employ a colorimetric method to measure the total ammonia in the water. Total ammonia refers to the free available ammonia plus the combined ammonia with chlorine. It is interesting to note that analyser 1 showed a decrease in the reading to around 0.1 mg/L in response to the addition of chlorine and the formation of monochloramine. This is hardly surprising as this analyser employs an ammonia selective electrode and only detects free ammonia. All analyser readings remained stable over a five hour period showing little if any variation.
Development of Tools for Improved Disinfection Control Within Distribution Systems

Figure 3.33 Response of ammonia analysers to ideal chlorine-to-ammonia ratio

Low and high chlorine to ammonia ratio
Figure 3.34 shows the results for the low and high chlorine to ammonia ratios for the ammonia analysers combined.

Figure 3.34 Response of ammonia analysers to low- and high chlorine-to-ammonia ratio

The analysers were exposed to a test solution containing 1 mg/L ammonia as N at the beginning of the experiment (time 0). The analyser output was allowed to stabilise and in the 70th minute, chlorine stock was dosed and mixed into the tank at a low chlorine-to-ammonia ratio (2:1) to form some chloramine and leave an excess of free ammonia residual in the water. This resulted in minimal impact on analysers 2, 3 and the reference instrument (Hach DR890), all of which are colorimetric analysers. However, a reduction in ammonia concentration was indicated by analyser 1 in response to the
reduced chlorine:ammonia ratio and this is explained as it employs an ammonia selective electrode technique which only detects free ammonia. All analysers stabilised to this sample water quality.

At the 270th minute the experiment for the 2:1 ratio was terminated and the analysers were exposed to water stored in tank B that had been dosed with an ammonia concentration of 0.5 mg/L. The analysers were allowed 30 minutes to stabilise and at the 300th minute, chlorine was added and mixed to the tank to achieve chlorine-to-ammonia ratio of 5:1. Readings from analysers 2, 3 and the reference instrument remained stable but the output from analyser 1 declined to <0.05 mg/L. This can be explained because at this chlorine-to-ammonia ratio (approximately 5:1), free ammonia should not be present. As previously indicated, analyser 1 measures only the free available ammonia.

At the 335th minute, additional chlorine was dosed and mixed to achieve breakpoint (chlorine-to-ammonia ratio 10:1) to completely oxidise ammonia. It can be seen that the analysers employing colorimetric measurement methods responded accordingly and showed a decreasing trend in ammonia concentration.

3.3.12 Summary of ammonia analysers results

Table 3.4 (p 142) summarises the performance demonstrated by the free and total ammonia analysers evaluated in this study.
3.4 Conclusions

The analysers evaluated in this study are representative of the current generation of commercial online analysers that are available in Australia. They are best suited for use in locations that have access to sample streams, instrument housing, a mains power supply, maintenance staff as well as sample disposal/recovery and chemical disposal facilities. The design as well as the installation and operating requirements of the analysers evaluated in this study makes their application in WDS not ideal and this adds considerably to the initial purchase cost of the instrument.

This trial was undertaken in laboratory conditions using new/relatively new and well serviced instruments. Results obtained are therefore "best case". The ISO standards 15839 (ISO 2003) and 8466-1 (ISO 1990) provide a rigorous frame work that can be used to evaluate the performance of online analysers. Few if any manufacturers make reference to these standards when reporting the performance of their instruments. For this reason, caution should be taken when benchmarking using performance data claimed by manufacturers as non-standard methodology may have been used.

The methodology used in this study requires considerable staff and equipment resources. It is recommended that prospective purchasers of online disinfectant residual analysers should determine the cost effectiveness of undertaking an evaluation trial using ISO 15839 (ISO 2003) and 8466-1 (ISO 1990) methodology.

The outcome of this project is to provide experimental information according to ISO Standard 15839 (2003), which can be used by a prospective end user of an analyser to identify how well this analyser performed in simulated laboratory conditions against the set of key performance characteristics. However, laboratory performance data and initial purchase cost are two of the many factors that should be considered. The authors of this report did not intend to specify which analyser/s performed well, and which did not, simply because field conditions for various end users may be different.

Many factors should be considered when selecting an online disinfectant residual analyser including initial cost of the analyser and installation facilities as well as cost of ownership (labour and replacement parts) in addition to KPI criteria. Potential users should consider the function of the analyser in ranking KPI. Response time (rise and fall) will be a primary criterion for control of chemical dosing but may be lesser importance if required for monitoring purposes only.

In order to make the best choice for an analyser, no single key performance parameter should be used, but their combination should be given a careful consideration with respect to real field conditions where this analyser is intended to be used, such as, type measurement, analytical quality, location of instrument, sampling requirements, data collection and transmission – SCADA, maintenance, calibration, quality assurance, operator training, and, the integration of online instruments into a water supply operating system (AWWARF 2002).
4 REFERENCES


5 APPENDICES

5.1 Techniques for the measurement of disinfectant residual

A range of colorimetric and electrode techniques are available for the measurement of free chlorine, total chlorine, monochloramine and free and total ammonia concentration online. Some methods are reagent-free, while others require the addition of a buffer or other chemicals. Several online analysers evaluated in this study use adaptations of standard methods of analysis (APHA 1998), and these are discussed in this report.

5.1.1 Online free and total chlorine methods

Online free and total chlorine measurement methods may be broadly defined as being either colorimetric or electrochemical.

DPD Colorimetric Method

The N,N-diethyl-p-phenylene diamine (DPD) colorimetric method is based on the Standard Method 4500-Cl G in which DPD is oxidised by free chlorine to form a red colour (APHA 1998). The colour intensity is proportional to the free chlorine concentration and can be measured spectrophotometrically. Free chlorine is measured at a pH level of 6.3-6.6, which is set by the addition of a buffer. For the determination of total chlorine, potassium iodide is introduced to the reaction of iodide-to-iodine oxidation by chloramines. Along with any free available chlorine, the DPD is oxidised to magenta colour at pH of 5.1, which is set by a buffer containing potassium iodide.

Polarographic Membrane Electrodes

These sensors consist of a pair of electrodes which are immersed in a conductive electrolyte and separated from a sample by a chlorine-permeable membrane. Chlorine diffuses through the membrane and is reduced to chloride on the surface of the electrode. This develops a flow of electrons and, consequently, an electric current proportional to chlorine concentration. Different membranes and electrolytes are used for free and total chlorine measurement. No reagents are required for this method.

Amperometric Electrodes

The amperometric method is a special adaptation of the polarographic principle. These instruments consist of two combination probes. The latter use a platinum cathode and a silver anode electrode for amperometrical measurement of residual free chlorine. Available free chlorine concentration effects an electrochemical reaction on these electrodes. No reagents are required for this method. This method can be related to standard method 4500-Cl D, Amperometric Titration Method (APHA 1998).

Iodometric Electrode Method

This method measures the direct potential of iodine released by the addition of potassium iodide to a water sample buffered at pH 4 to react with available chlorine compounds to form an equivalent amount of iodine. The current is monitored by a pair of electrodes, and can be correlated to the amount of available chlorine. This method can only be used for total chlorine, and is based upon the standard method 4500-Cl (APHA 1998).

Galvanometric Electrode Method

An external voltage is applied to a galvanic cell to measure the concentration of particular species. Gold is used as an electrode, and as a reference electrode is used a silver/silver chloride electrode. Chlorine and monochloramine can be measured using a three-electrode voltametric technique. The electrodes electrochemically adjust sample pH, which stabilises the chlorine measurement against ambient pH changes and acts as an anti-fouling measure.
5.1.2 Online monochloramine methods

Phenate method

Monochloramine may be measured online using a colorimetric method. This method is similar to the phenate method for ammonia described later, except that hypochlorite solution is not added. The method used in analyser evaluation program is a slight variation on the method described in Standard Methods (APHA, 1998). Sodium nitroprusside is used as the catalyst, instead of a manganous salt which is used in the standard method 4500-NH₃.

In the analyser method, monochloramine present in the water sample react with a phenol reagent in an alkaline medium; tri-sodium citrate and ethylene-diamine-tetra-acetic acid (EDTA) are added to the sample to avoid the precipitation of alkaline hydroxides, while nitroprusside acts as a catalyst intensifying the blue colour produced (Indophenol blue) which is measured at 630 nm colorimetrically.

5.1.3 Online free and total ammonia methods

Free and total ammonia in water is usually measured online using ion selective electrode or colorimetric techniques. Two methods employed by analysers evaluated in this study are described below.

Free ammonia - ion selective electrode method

Free ammonia can be measured using potentiometric techniques employing a specific ion meter as described in standard method 4500-NH₃-F (APHA 1998). Ammonia-selective electrode techniques require the sample to be buffered to pH >11 with a strong base, NaOH, to convert all ammonium ions, NH₄⁺, presented in water sample to ammonia, NH₃. The electrode itself uses a hydrophobic gas-permeable membrane to separate the sample solution from an electrode internal solution. Ammonia, NH₃, diffuses through a membrane, and changes the internal solution pH that is detected by a pH electrode. The fixed level of chloride in the internal solution is determined by a chloride ion selective electrode, which acts as the reference electrode. The change of the pH and the value of the reference electrode are correlated to the concentration of free ammonia in the sample.

Total ammonia - phenate method

A modified colorimetric method, 4500-NH₃-F (APHA, 1998), based on the standard methods 4500-NH₃-D & -H (APHA, 1998) can be used to measure total ammonia online. In this method used by many online analysers, intensity of a blue compound, indophenol, formed by the reaction of ammonia, hypochlorite, and phenol catalysed by sodium nitroprusside is measured colorimetrically. Tri-sodium citrate and EDTA are added to the sample to avoid the precipitation of alkaline hydroxides, while nitroprusside acts as a catalyst intensifying the indophenol blue colour produced. The colour intensity is proportional to the concentration of total ammonia in the sample, and is measured at 630 nm colorimetrically.
5.2 Description of the online analysers evaluated

This chapter gives an overview of the analysers evaluated in this trial and their technical features. Instrument suppliers were responsible for installing their analyser in the test rig commissioning. They also trained the research personnel in the operation of their analyser. Most analysers were relatively new and given that they were evaluated under laboratory conditions, may mean that performance results obtained are "best case". Analyser performance may deteriorate as the instrument ages and if harsh operating conditions are used.

Four types of analyser, based upon disinfectant residual type, were evaluated in this study: free chlorine, total chlorine/monochloramine, free ammonia analysers, total ammonia analysers, and multiparameter analyser.

The information used to describe these analysers has been obtained from analyser manuals or from instrument suppliers.

5.2.1 Free chlorine analysers

The following free chlorine online analysers were evaluated:

- Endress & Hauser CCS141;
- HACH CL17;
- B&C Electronics CL 7685;
- Yokogawa model FC400G-63*A/Z;
- Wallace & Tiernan - Depolox 3 plus (membrane style);
- Wallace & Tiernan - Depolox 3 plus (bare electrode style);
- ATi Model A15/62; and
- Prominent Dulcotest sensor-type CLE and Dulcometer D1C.

**Endress & Hauser CCS141**

The Endress & Hauser CCS141 free chlorine sensor (Fig 3.35) was supplied with a CCA250 flow assembly and Liquisys M CCM253 transmitter (Endress+ Hauser Australia Pty Ltd. NSW). The analyser has a free chlorine measurement range of 0–5 mg/L but this was adjusted to 0–2 mg/L to bring it inline with the conditions used in this trial and to improve resolution.

The CCS141 sensor is a membrane covered amperometric trace sensor that uses a gold cathode and a silver anode. It detects only hypochlorous acid, free chlorine is determined by simultaneously measuring temperature and pH. Hypochlorous acid (HOCL) present in the sample diffuses through the membrane and is reduced to hydroxide (OH⁻) and chloride (Cl⁻) ions. The chloride ions oxidise the silver anode to produce silver chloride and generate a current in proportion to the hypochlorous acid concentration.
The flow assembly CCA 250 (Figure 3.36) has an optical flow monitoring system, which can trigger an alarm in the absence of flow. The flow assembly has a minimum flowrate requirement of 30 L/h. Above this value, the measurement is almost independent of the flowrate. No zero point calibration is required for this instrument. Electrolytic conductivity does not affect the measurement, and pH compensation is built-in with a range from 4 to 9. Both, pH and electrolytic conductivity were applied as interferences in the testing procedure to verify these claims. This analyser is capable of displaying values of pH, free chorine or chlorine dioxide concentrations, as well as providing alarm signals, which can be set for chlorine limits.

Calibration of both the sensor and the pH probe is required at regular intervals. The chlorine electrode requires calibration twice yearly and the pH electrode requires calibration at least three times per year. Manufacturers indicate that the membrane, chlorine electrode and pH electrode require replacement every 2, 7 and 1.5 years, respectively. The unit has a 4-20 mA output, and a series of alarms are available for user definable high-and low-chlorine set-points, the length of time the alarm has been activated and also for monitoring signal change.
Hach CL17

The HACH CL17 (Figure 3.37) is a microprocessor controlled analyser designed to monitor either free or total chlorine in the range of 0–5 mg/L, depending on the buffer and indicator solutions used (Hach Company, Loveland Co, USA, supplied by Biolab, Victoria). The unit is not designed for outdoor use and therefore requires a suitable housing. The instrument uses a colorimetric DPD technique with a buffer.

![Figure 3.37 Photo of HACH CL17](image)

For the determination of free chlorine, the indicator and a buffer are mixed with the sample producing a red colour if chlorine is present. Free chlorine oxidises the indicator in a pH range of 6.3 – 6.6. The buffer solution maintains the correct pH, and the analyser is therefore independent of sample pH. The intensity of the red colour is proportional to the chlorine concentration. The reagents require changing once a month and can be obtained from the instrument suppliers. A sample is taken every 2.5 minutes and the blank absorbance is measured and used to compensate for the presence of turbidity or natural colour in the sample and to provide an automatic zero reference point. A linear peristaltic pump is used to flush tubing and the sample chamber and deliver sample and reagents to the chamber.

The unit has a 4–20 mA output and alarm triggers at designated low and high chlorine concentrations. A system alarm and system warning is also available. Manufacturers indicate that standard maintenance tasks can be easily performed, including priming and cleaning the system as well as replacement of peristaltic pump tubing. Also, depending on sample conditions, the colorimeter will require cleaning. Manufacturers recommend a monthly cleaning frequency using an acid solution and a cotton swab. The instrument does not require calibration unless specified by a regulatory agency for compliance reporting.

This unit was found to be very simple to use, but care must be taken that the reagents do not exceed their expiry date or run out as this will produce incorrect readings.

B&C Electronics CL 7685

A system comprising a B&C Electronics CL 7685 model potentiostatic controller (Carnate, Italy, supplied by Accurate Detection, NSW) with a SZ 283 potentiostatic electrode and SZ 7231 flowcell for free chlorine measurement was evaluated (Figure 3.38). Readings produced are highly dependent on the flow, and it is very important that the flow to the sensor is constant.
Manufacturers explain that the analyser employs an amperometric technique that measures at a constant potential using a three-electrode measuring system consisting of two metal electrodes (measuring and counter) and a reference electrode. The model SZ 283 has platinum measuring and counter-electrodes for reduced corrosion. The reference electrode has the gel electrolyte to provide a good liquid contact and low electric resistance. The two metallic electrodes are both ring shaped, with the measuring electrode placed at the top and the counter electrode at the bottom.

The analyser is claimed to have two measuring ranges 0–2 mg/L and 0–20 mg/L. The 0–2 mg/L range was selected for this trial. The unit requires a span calibration only and so does not require a zero setting. Temperature compensation is an additional feature of this unit. Free chlorine readings are dependent upon pH variations and this can be controlled using a CO₂ gas buffering sparger. Manufacturers claim that maintenance is limited to cleaning of the probe and flow cell. The sensor is very simple to clean and replace. The unit has a 0-20 mA or 4-20 mA output signal for data logging.

Yokogawa Model FC400G-63*A/Z

The model FC400G-63*A/Z (Figure 3.39) is a non-reagent type free chlorine analyser with pH compensation in the range 5-9 pH (Yokogawa Australia Ltd, NSW, supplied by Amec, Adelaide, SA). It measures free chlorine in the range 0–3 mg/L using a polarographic rotating gold electrode that is continuously cleaned by the action of rotating ceramic beads. The analyser has a silver reference electrode. A sample temperature should be in the range of 0-50°C. Flowrate should be within the range 0.1–2.5 L/min and this can be adjusted using the flow cell provided. Electrolytic conductivity of a sample should be in the range 100 to 300 µS/cm.

This analyser is designed for use in a building, exposure to direct sunlight is not recommended. A weather proof cover is required if the analyser is installed outdoors. The unit can be calibrated using a zero and span input. The zero is done by simply removing the probes from the solution, and zeroing in air.
Manufacturers claim that maintenance is limited to manually polishing the gold electrode. The measuring tank and ceramic beads also require to be cleaned regularly. Several errors can be automatically indicated ranging from those occurring during measurement, maintenance, and during data setting.

**Wallace & Tiernan - Depolox 3 plus (membrane style)**

The membrane style Wallace & Tiernan - Depolox 3 plus free chlorine residual analyser (Wallace and Tiernan, NSW, supplied by Hydramet (SA) Pty. Ltd., Edwardstown S.A) uses an amperometric membrane (Figure 3.40). Free chlorine is measured using a three-electrode cell with an external potentiostatic closed loop system. The working and reference electrodes are made of platinum alloy, and the reference electrode is a silver/silver chloride electrode. There is a constant adjustable potential between working and reference electrodes by means of a potentiostatic closed-loop control. An electrical current generated in the cell is proportional to a free chlorine concentration in the sample, and is passed on to the microprocessor-based control electronics. No zero adjustment is required, and turbidity and conductivity do not affect the calibration or accuracy of this instrument.

*Figure 3.39* Photo of Yokogawa Model FC400G-63*A/Z.
This analyser has a measuring range of 0–20 ppm. The probe is placed in a plexiglass flow-block assembly, which controls the flowrate in the range of 6-35 L/hour. Sample water quality should be in the range 5–45°C (temperature), 10-2500 µS/cm (conductivity), and 6-10 (pH). This unit has a dual input for pH measurement offering pH compensation. Low and high alarms are available for chlorine and pH measurements. It also has a 4–20 mA output that corresponds to the above free chlorine measuring range. Manufacturers claim that the membrane and electrolyte should be replaced once and twice per year, respectively.

**Wallace & Tiernan - Depolox 3 plus (bare electrode style)**

The Wallace and Tiernan – Deploox 3 bare electrode style analyser (Wallace and Tiernan, NSW, supplied Hydramet (SA) Pty. Ltd., Edwardstown S.A) measures free chlorine using an identical 3-electrode sensor to that used by the membrane covered unit described previously. Manufacturers indicate that the bare electrode is only capable of measuring free chlorine and is best suited to applications requiring a quick response time or if there is high hardness in the sample water that could foul a membrane sensor. A second sensor can be added if pH or fluoride measurement is required. The bare electrode style is affected by pH changes, however pH compensation is available.

The electrodes are mounted in the lower part of a plexiglass body and are automatically cleaned using grit (Figure 3.41). Both the membrane and bare electrode analysers consist of a flow through cell with a transparent plexiglass body that houses the sensor. This analyser provides a variety of measuring ranges from 0 to 20 mg/L. The range used in this trial was 0–5 mg/L. A sample flow of approximately 33 L/h should be maintained and a sample pH within the range 4-9 pH is required. Sample temperature should be within the range 5–50°C with conductivity >250 µS/cm.
The unit has a 4-20 mA output, two freely configurable alarm contacts for disinfectant signal, and an RS-485 for connection to programmable controller or central instrumentation and control systems. Manufacturers claim that maintenance consists of visual checks for leaks and ensuring that there is sufficient grit in the flow cell, cleaning the strainer in the sample water supply line and checking the zero point. The reference electrolyte should be changed once in six months.

**Analytical Technology, Inc. ATi A15/62**

The Ati A15/62 residual chlorine monitor was evaluated (ATi, Oaks, PA, USA, supplied by Hydramet (SA) Pty. Ltd. Edwardstown S.A). The instrument has a measuring range of either 0–2 mg/L or 0–20 mg/L of free chlorine and is a reagent-free polarographic membrane sensor. It consists of a pair of electrodes immersed in a conductive electrolyte that are isolated from the sample by a chlorine-permeable membrane (Figure 3.42). Chlorine migrates through this membrane by diffusion, and is reduced to chloride on the surface of the working electrode. This causes a flow of electrons through an external measuring electronic circuitry, with the value of electrical current being linearly proportional to chlorine concentration. Automatic temperature compensation is also provided.
Two 4-20 mA outputs are provided for data recording or data logging, one output for chlorine and the other for temperature. Alarm contacts are also provided as a standard configuration in the electronic package and they may be used either for simple control schemes or for alerting operators to abnormal operating conditions. The A15/62 system includes a panel mounted electronics unit, a constant head flow cell, and a free chlorine sensor. Sample temperature should be within 5 to 55°C.

For reliable operation, the sensor should be maintained on a regular basis. Manufacturers claim that almost all maintenance is sensor-related as the electronics are generally trouble free. Keeping the membrane clean is the main requirement, and this should be replaced every three months. O-rings should also be monitored and changed annually. The sensor can be acid cleaned to remove deposit build-up on the surface of the platinum electrode. The flow cell should be kept clean.

**Prominent Dulcotest CLE and Dulcometer D1C**

A system comprising a Prominent Dulcotest CLE sensor and a Dulcometer D1C measuring transducer/controller (Figure 3.43) was evaluated as part of the free chlorine trial (Prominent, Belrose, NSW, supplied by All Pumps Supplies, Edwardstown SA). The sensor is a membrane covered, amperometric design comprising two-electrodes. A variety of ranges are available from 0-10 mg/L. Manufacturers claim that the instrument can operate within a samples pH range of 5.5 to 8.5 and a temperature range of 1-45°C. The system includes temperature measurement integrated into the lower end of the electrode shaft allowing temperature compensation. It is also claimed that electrolytic conductivity does not affect free chlorine measurement within the range 50 to 10,000 µS/cm. The recommended sample flow rate through the flow cell is 40-60 L/h.
Maintenance involves cleaning the sensor, replacing the membrane cap and checking the sensor display value on the controller using an appropriate chlorine measuring system (DPD-1). The manufacturer’s claimed membrane cap life is one year and analyser calibration frequency is once a month. The unit has a two standard 4-20 mA outputs and has the ability to be used as a PID controller or as a feed forward controller.

5.2.2 Total chlorine and monochloramine

Five total chlorine/monochloramine analysers were evaluated in this study and four analysers are described in this section:

- Analytical Technology, Inc. – ATi Model A 15/63;
- Prominent – Dulcometer 1;
- Wallace & Tiernan – Depolox 3 plus; and

The multiparameter Systea analyser measures total chlorine and monochloramine and is described later.

Analytical Technology Inc. –ATi 15/63

The Ati 15/63 measures total chlorine in the range 0-20 mg/L using a polarographic membrane sensor. (ATi, Oaks, PA, USA, supplied by Hydramet (SA) Pty. Ltd., Edwardstown SA). A measuring range of 0 to 2 mg/L was used in this trial. The electrode is housed in a constant-head overflow to control variations in sample flow rate and pressure. The sensor does not require the addition of regents for measurement or cleaning during normal operation. Calibration consists of adjusting the analyser to match titration results for total chlorine. The analyser provides two analogue output signals that can interface with recorders, data loggers, or controllers. Each analogue output is programmable for either 0-20 dc or 4-20 mA output. This unit is also equipped with three relay outputs. Two of these outputs are designated control relays, and can be used in three different output modes, such as, on/off, pulse with modulation, and pulse frequency modulation. This allows using the above relays for either alarm functions or control functions. The third relay is designated as an alarm relay, and may be provide warning of low or high chlorine concentration.
Prominent – Dulcometer 1

The Prominent Dulcometer 1 (Prominent, Belrose, NSW, supplied by All Pumps Supplies, Edwardstown SA) is a reagent free membrane covered 2-electrode amperometric continuous total chlorine analyser that has a range of 0 to 10 mg/L (Figure 3.44). A range of 0 to 2 mg/L was used for this evaluation. Calibration consists of adjustment to match a titration results. The sensor is equipped with temperature compensation and can be used in the pH range 5.5 to 9.5. A pH sensor can be included allowing pH compensation to be made.

Figure 3.44 Photo of Prominent – Dulcometer1.

Manufacturers claim that maintenance is limited to the sensor and sensor cell. The sensor requires regular checks against a laboratory measurement and if necessary recalibration. If the membrane is contaminated, it can be cleaned under a soft, cold water jet or re-placed. The analyser provides two analogue output signals. Each analogue output is programmable for either 0-20 mA or 4-20 mA output. The analyser has the ability to be used as a proportional controller, as a PID controller or as a feed forward controller. This allows the analyser to control devices for example pumps for pH control or disinfectant dose. For controlling use a free programmable analogue input signal or a digital contact signal with the maximum frequencies 10 or 500 Hz can be used to control two frequency outputs (e.g. for pump activation).

Wallace & Tiernan (W&T) - Depolox 3 plus

The Wallace & Tiernan Depolox 3 plus previously described (Wallace and Tiernan, NSW, supplied by Hydramet (SA) Pty. Ltd. Edwardstown SA) can also continuously measures total chlorine in the range 0 to 20 mg/L. Seven different measuring ranges can be selected (0 to 0.2, 0.5, 1, 2, 5, 10 and 20 mg/L) and the range used in the evaluation was 0 to 5 mg/L. This analyser consists of two separate components, a flow-through sampling cell housing a 3-electrode-amperometric membrane covered sensor and the electronic package. Different electrodes are available to measure a range of oxidants including free chlorine, total chlorine, chlorine dioxide and ozone. A second sensor can be added for pH or fluoride measurement. The sensor is equipped with temperature compensation and a pH range of 6 to 9 can be used. Optionally, pH compensation is possible using a second pH sensor.
The operating manual recommends a maintenance schedule that includes daily, weekly, bimonthly and semi-annual checks for calibration and cleaning. The membrane itself cannot be cleaned and typical replacement frequency is three years however this may reduce if water quality is poor. The analyser provides an analogue output with 4 to 20 mA analogue output, and two freely configurable alarm relays for each connected sensor that can be set to high and low concentration set point, general fault or activation by digital input and dosing control. Additionally, the analyser is equipped with a RS-485 interface for data transmission, and a digital input.

**Applikon – Alert 2004**

The Applikon Alert 2004 (Aplikon, Schiedam, Netherlands, supplied by MEP Instruments Pty Ltd., North Ryde, NSW) measures total chlorine in the range from 0 to 2.5 mg/L. The analyser operates in a batch cycle and uses a colorimetric method (based on the DPD colorimetric method). The analysis sequence consists of sampling, analysis and result processing. The analyser is built as one unit consisting of an electric part, including human interface and in-interface, input and output connections and the wet part, where the analysis takes place (Figure 3.45). The wet part includes peristaltic pumps for sample transfer and reagents dosing, tubing, valves and the colorimetric measuring cell.

The analyser uses two reagents to measure total chlorine, a buffer solution and DPD solution. Buffer is added to the sample, stirred for 60 seconds and the initial absorbance value is measured. DPD colour solution is then added and the final absorbance value is determined after a reaction time of 60 seconds. After measurement, the total chlorine concentration of result is displayed on the screen. The analyser range can be adjusted by determining a calibration curve that is ten times higher than the actual top end of the measuring range. A blank solution and four standard solutions ranging up to 100% of the calibration range are required for the first calibration. During normal operation, an automatic zero calibration using distilled water is undertaken.

![Photo of Applikon – Alert2004.](image)

The manufacturer claims that maintenance involves changing or refilling the reagent containers and checking the wet part in case of leakages etc. The pump tubing should be replaced and the cuvette of the colorimeter should be cleaned at regular intervals (at least once a year). The analyser operates in three programmes: analysis, reference and cleaning. While the analysis programme is always used to
measure, the cleaning and reference programme can be operated by an adjustable ratio automatically (programmable macro). The analyser provides one programmable analogue output with a signal from 0/4 to 20 mA dc; a second analogue output is optional. Three free programmable output relays can be activated by a programmable macro or by a manual command. They are used to read the status of the analyser in other devices or to drive an indicator lamp, buzzer or other small devices. In addition, four alarm relays can be programmed for power on alarm, processing alarm and two result alarms. Serial communication connections modules RS232/422 are optional RS-232/422 are available.

5.2.3 Free and total ammonia analysers

Three commercial free and total ammonia analysers were evaluated in this study, and two of these are described in this section:

- Applikon - ADI 2018 HD;
- Endress & Hauser – StamoLys CA 71 AM; and

The third ammonia analyser evaluated was manufactured by Systea (MP4 MicroMac C Analyser) and is described in the multiparameter section.

**Free ammonia analyser - Applikon – ADI 2018HD**

The Applikon ADI 2018 HD analyser (Aplikon, Schiedam, Netherlands, supplied by MEP Instruments Pty Ltd., North Ryde, NSW) is an online batch free ammonia analyser that has a range from 0.2 up to 10000 mg/L (Figure 3.46). The analyser uses an ion selective electrode (ISE) as part of a dynamic standard addition method. The range of the analyser can be adjusted by using different calibration solutions and was calibrated up to 1 mg/L for this evaluation. This analyser is similar to the Applikon total chlorine analyser; it is built as one unit separated into an electronic part including a human interface and input-output connections and the wet part where the analysis takes place. The wet part includes peristaltic pumps for sample transfer and reagents dosing, tubing, valves and the ISE. The principle of the batch analysis involves a sequence of sampling, analysis and result processing. The analyser uses one reagent (total ionic strength adjustment buffer (TISAB) solution) to measure free ammonia. High grade distilled water is used for rinsing between the analysis and the zero signal. After sampling the TISAB solution is added to the measuring cell to increase the pH of the sample and convert ammonium ions, NH₄⁺, to ammonia, NH₃, and these are measured using the ISE.

**Figure 3.46** Applikon ADI 2018.
The basic maintenance of the analyser is similar to the total chlorine Applikon analyser. It involves changing or refilling the reagent containers and checking the wet part for leaks. The pump tubing and the glass cylinder and piston in the burette module require regular replacement (at least once a year). The recommended way to maintain the electrodes is to alternate between two identical sets of electrodes on a regular base (e.g. monthly). One set can be cleaned and reconditioned, while the other set is installed in the analyser.

The programmable operation is similar to the Applikon total chlorine analyser, there are three possible programmes: analysis, reference and cleaning. The analysis programme is all ways used to measure, the cleaning and reference programme can be operated by programmable automatic programme. The analyser provides one programmable analogue output with a signal from 0 to 20 dc and 4 to 20 mA; another two analogue outputs are optionally available. One free programmable output relay can be activated by a programmable macro or by manual command, and is used to read the status of the analyser in other devices or to drive an indicator lamp, buzzer or other small devices. In addition, four alarm relays can be programmed for power on alarm, processing alarm and two result alarms. Serial communication connections modules RS-232, RS-422 and RS-485 are optional available.

**Total ammonia analyser - Endress & Hauser - StamoLys CA 71 AM**

The Endress and Hauser – StamoLys CA 71 AM analyser (Endress+ Hauser Australia Pty Ltd. NSW) is a batch free ammonium ion analyser with a range up to 100 mg/L (Figure 3.47). It uses a colorimetric technique (indophenol blue method acc. ISO 11 732). The analyser has four ranges that can be selected: 0.1-5 mg/L, 0.2-15 mg/L, 0.5 to 100 mg/L and 1 to 500 µg/L of NH₄-N. The range 0.1-5 mg/L of NH₄-N was used for this study. One measuring cycle takes about 5 minutes, depending on the sampling time. After the cycling period, the result is showed in mg/L of NH₄-N on the display until the next reading is available.

The analyser is built as one unit with an overflowing sampling cell attached on the side of the analyser. The electronic part of the analyser is in the upper part of the unit and includes the display, human interface, inputs and outputs and is separated from the wet part. The wet part includes peristaltic pumps for sample transfer and reagent dosing, tubing, valves, the reagents bottles and the colorimetric measuring cell. To measure free ammonium ions, two reagents and a calibration and cleaning solution are required and these can be obtained from the supplier. The analyser sample pump conveys the sample to the mixing vessel. The reagent pumps add reagents at a specific ratio to the sample. In the presence of free ammonium ions, a characteristic blue colour is formed. The photometer determines the absorption of the sample which is proportional to the concentration of free ammonium ions. In addition, the absorption of a reference light is determined by a received reference signal, which value is subtracted from the measuring signal to prevent any effects due to turbidity, contamination and ageing of the light emission diodes (LED). An auto-calibration and cleaning cycle of the analyser can be done manually or at set time-intervals. An interval of up to 72 hours is recommended for recalibration below 30°C. At temperatures above 30°C, recalibration is needed every 6 hours.
This analyser provides one programmable analogue output with a signal ranges from 0-20 mA dc and 4-20 mA dc, and three output relays. Two relays are programmable to give alarm for high- and low-limits, whereas the third relay signals a system alarm. An RS-232 serial interface communication connection is standard in this analyser.

5.2.4 Multiparameter analysers

**Systea – MP4 MicroMac C Analyser**

The Systea MP4 MicroMac C (Systea, Anagni, Italy), a multiparameter colorimetric analyser (Figure 3.48) was evaluated in this study. This analyser has the ability to sequentially measure total chlorine, monochloramine and total ammonia. The measuring range for free and total chlorine is 0 to 6 mg/L, and for total ammonia and monochloramine is 0 to 2 mg/L. The sample time for total ammonia and monochloramine is approximately 8 minutes each and free chlorine and total chlorine require 6 minutes each. The total time for a complete analytical cycle is approximately 30 minutes however each individual measurement can be activated on request by the user. If the measuring (monitoring) function is active, the system will wait until the expiry of the interval time and then will than start a new cycle otherwise the system will stay in the ready-mode and an analysis can be started at any time. A number of reagents are required for each parameter. Total ammonia and monochloramine measurement is based upon the phenate method previously described and requires, chlorine, dichloroisocianuric acid sodium salt (DIC) and sodium hydroxide. Free and total chlorine is measured using a modified DPD method employing a buffer, DPD and potassium iodide solution. In addition, standard calibration solutions for ammonia and chlorine are also necessary for calibration.
The analyser employs the same operating principle for all four parameters methods. The sample is aspirated by the internal pump and dosed in a specific portion of the hydraulic circuit. The colorimeter is zeroed with the sample in the flow cell, at the specific wavelength required by the method. The reagents of the specific chemistry are added, and the reaction takes place inside the hydraulic circuit. The measurement of the optical density is undertaken and the concentration is calculated. The system is washed with diluted water to remove all traces of the reaction products and proceed to the analysis of the next parameter. After the last parameter is analysed, the system is ready for a new cycle.

Up to 400 results can be stored in the internal memory allowing 100 results per determinand and these can be exported as 4-20 mA output. Analogue outputs are logged using a different data logger that is linked to the analyser using a different interface. Manufacturers claim that maintenance is limited to replacement of reagents, replacement of the peristaltic pump tubing every six months and replacement of silicon tubing where the chemical reactions take place at yearly intervals. The system operates from an electrical source of 12 V dc with low power consumption, making it possible to operate the system by a battery and/or a solar panel. For a particularly hot environment, a special reagent compartment fitted with a Peltier cooling device is available.

5.3 Experimental methods
This chapter gives an overview of the test rig design and operation, data logging and the laboratory analytical methods used in this trial.

5.3.1 Analytical methods
The following laboratory-based methods were used to determine the concentration of residual disinfectant (chlorine, monochloramine, total chlorine or free and total ammonia) supplied to the analysers in the test-rig.
Free chlorine, monochloramine and total chlorine

Free chlorine, chloramine (monochloramine and dichloramine) and total chlorine concentration were determined using a titration method (APHA, 1998). The method has a range from 0.03 to 5 mg/L of total chlorine. The principle of the method is as follows: DPD is used as an indicator in the titrimetric procedure with ferrous ammonium sulphate (FAS) at a pH 6.2–6.5 (5). For a 100 mL sample, 1 mL FAS is equivalent to 1 mg/L of residual chlorine.

Free available chlorine reacts instantly with DPD indicator to produce a red colour, and this is titrated with FAS to give free chlorine concentration ($c_1$). Subsequent addition of a small amount of iodide acts catalytically to cause monochloramine to produce colour. Titration is resumed with the FAS until the endpoint ($c_2$), and the monochloramine concentration is calculated as ($c_2-c_1$). Then, addition of excess iodide to the sample causes a rapid response from dichloramine. Titration with the FAS to the endpoint ($c_3$) allows the concentration of dichloramine to be calculated as ($c_3-c_2$). Combined chlorine can be calculated as ($c_3-c_1$). Total chlorine is equal to the sum of free chlorine, monochloramine and dichloramine, and is represented by $c_3$.

Total ammonia.

The Hach DR 890 hand held multiparameter unit (Hach Company, Loveland Co, USA) was used to measure total ammonia in the 0-2.5 mg/L range (as NH$_3$-N). The unit is a micro-processor controlled, LED-sourced filter photometer that is suitable for colorimetric testing in the laboratory or field. The low range total ammonia method, referred to as the salicylate method, uses ammonia salicylate and ammonia cyanurate as reagents. A twenty-minute reaction time is required for colour development prior to measurement using a colorimeter.

The manufacturers indicate in the method that ammonia compounds combine with chlorine to form monochloramine. Monochloramine then reacts with salicylate to form 5-aminosalicylate, which is oxidised in the presence of a sodium nitroprusside catalyst to form a blue-colour compound. The blue colour is masked by the yellow colour from the excess reagent present to give a final green coloured solution. The method is based on the indophenol method.

5.3.2 Test rig

Test rig design

A test rig was constructed to supply all analysers under evaluation with a continuous water sample having an equivalent quality (Figure 3.49). The rig included three water tanks (labelled A, B and C. Tanks A and B were used to prepare and store a preset concentrations of chlorine or ammonia and tank C always contained chlorine-free and ammonia-free water. Each tank was equipped with a submersible pump. Pumps 1, 2 and 4 delivered water to the analysers and pump 3 carried water from tank C to tank A, when necessary. The analysers were connected in-line using a manifold.

Water could be recirculated from the storage tanks to the analysers and the recirculation flow rate was measured using an inline rotameter installed after pump 4 and adjusted using valve 13. Water from analysers that did not adulterate the sample by chemical addition was returned to tank A or B by adjusting valves 7 and 8. Water adulterated by chemical addition was disposed to the drain after measurement. Valves 14 to 21 were used to isolate analysers when required for trouble shooting or maintenance.
Figure 3.49 Test rig design.

Test rig operation

During the evaluation, valves 1, 2 and 3 were closed to prevent mains water from entering the system.

Various concentrations or solutions were prepared and stored in tanks A and B depending on the evaluation test. Tank B contained the blank solution and tank A contained the test solution. Valves 5 and 6 are used to change the water inlet from tank A to B or reverse. To prevent mixing of the two solutions in the tanks, valve 7 and 8 in the flow back line were closed and valve 12 was opened to the drain to allow the recirculating system to flush out any other solution before it runs back into the tank. This procedure was carried between all concentration changes.

Overnight the rig was kept in a “standby position” and all analysers remained in operation as normal except for batch type analysers where the sampling interval was set to maximum to reduce chemical usage. Tank A was always used for standby and it was equipped with a float valve (V-4) that maintained a fixed level in the tank over night by adding tap water as necessary. Water was supplied from Little Para WTP, South Australia. Water quality data is shown in the appendices. Tanks B and C were always filled with tap water and stirred overnight allowing free chlorine to dissipate. Dechlorinated tap water was used as a blank and to dilute the sample if an overdose occurred the following day.

Sample Preparation

Analysers sample water quality was prepared in batches by dosing chemical reagent(s) to dechlorinated water stored in tanks A, B or C. Tap water was used to prepare the blank and sample solutions. All free chlorine residual was allowed to decay to <0.1 mg/L after 12 hours storage and continuous stirring in the tanks, however there was still a small amount of dichloramine remaining (max. 0.1 mg/L).

Free chlorine samples were prepared by dosing sodium hypochlorite solution (1mg/mL free chlorine). Free chlorine analysers were evaluated within the range 0-2 mg/L (0%-100%). Because of the presence of the dichloramine, all chlorine/chloramine components were measured by titration to ensure compatibility with the total chlorine analyser readings.
Standard monochloramine test solutions were prepared by dosing pre-formed monochloramine solution (725 mg/L as monochloramine NH₂Cl prepared every two to three days) to dechlorinated water that had been pH corrected to 8.0 using sodium hydroxide. Samples having low and high chlorine to ammonia ratios were prepared by dosing and mixing ammonia followed by sodium hypochlorite and mixing to dechlorinated water that had been pH corrected to 8.0 using sodium hydroxide. Monochloramine analysers were evaluated in the range 0 (0%) – 2 (100%) mg/L.

Total chlorine is the sum of the free chlorine and chloramine concentration. As there was no free chlorine present in the standard monochloramine sample, the total chlorine was the same as the monochloramine concentration.

The working range of the ammonia trial was 0 (0%) to 1 mg/L of NH₃-N (100%). The ammonia sample concentration was adjusted by adding ammonia stock (1000 mg/L NH₃-N) to pH corrected (8.0) dechlorinated water stored in the test-rig tanks and mixing.

Verification of all sample disinfectant residual concentration was determined regularly by performing laboratory analysis. At each concentration, the ammonia concentration was measured three times (in duplicate) with the Hach DR 890 hand held unit and titrated twice (in duplicate).

5.3.3 Data logging

The output from individual analyser and the corresponding time and date was logged using a data logger (Figure 3.50) (Measurement Engineering Australia Pty. Ltd. Magill, South Australia). Individual analysers standard output signal between 4 and 20 mA and this corresponded to the measuring range used. The recorded values of the data logger unit were proportional to the concentration of chlorine or ammonia measured by the analysers.

A preliminary response time (PRT) test (see later) was undertaken to establish the required logging frequency of the data logger to enable the analyser performance characteristics to be determined.
The data logger unit was connected via RS-232 interface to a personal computer. This computer was used also to program the data logger and to monitor individual analyser output in real time. The software programme Magpie (Measurement Engineering Australia Pty. Ltd, Magill, South Australia) was used to calibrate the analyser output signals (4–20 mA) to the measuring range of each analyser. As an example, Figure 3.51 presents a screenshot of the setup menu for the Atl analyser.

Temperature and the pH of the test solution were also logged to the data logger. A thermocouple converter (80TK Thermocouple Module manufactured by FLUKE) was used to measure water temperatures and pH was measured using the online pH meter included in the Prominent Dulcometer 1 free chlorine analyser.
5.4 Online analyser key performance indicators explained

This section provides background to the key performance indicators that are used in this report. It explains the terms and definitions and it provides details of the calculations that were used to determine the following key performance indicators: response, delay, rise and fall times; linearity; coefficient of variation; limit of detection; limit of quantification; repeatability and day-to-day repeatability; lowest detectable change; bias; short-term drift; memory effect; and interferences (pH, conductivity, etc.).

5.4.1 Response, delay, rise and fall times

The response of an online disinfectant residual analyser to variation in disinfectant residual (free chlorine, total chlorine/monochloramine or ammonia concentration in water) should be as quick as possible. If an analyser responds quickly to these changes, then it is well suited to process control applications. If an analyser demonstrates a slow response then it may be only suitable for monitoring applications.

For a better understanding of what response, delay, rise and fall time mean, a typical response from an online analyser to an abrupt change in disinfectant residual concentration is shown in Figure 3.52. In this example, data points were collected at certain time intervals. In order to obtain the function of the analyser’s response, the collected data points were plotted and approximated by analytical equations using the program Table Curve (reference needed) that correlates concentration readings versus time. The function $f_1(t_1; t_2)$ (red line) begins at $t_1$ when the concentration is changed to 100% of the working range and ends at $t_2$ when the concentration is changed back to 0%. At this point the next function $f_{n+1}(t_3; t_4)$ begins and ends with the next change of concentration.

Figure 3.51 Screenshot of Magpie data logging software.
Figure 3.52 Typical on-line analyser response to an abrupt change in determinand value.

Examples

A number of examples showing how to calculate the response time, delay time, rise time and fall time, arbitrary chosen examples are provided in following text. The smaller the response, delay, rise and fall time for an analyser, the quicker that it will respond to a change in disinfectant residual concentration. A data logger records readings produced by an online disinfectant residual analyser and corresponding time. The recorded data is presented in graphical or analytical (equation) form (Figure 3.53). It is assumed that the analyser readings are equal to actual disinfectant concentrations obtained from laboratory analysis. In this example, the concentration of disinfectant residual exposed to the online analyser was increased from 1.0 mg/L to 2.0 mg/L and then decreased to 1.0 mg/L over a period of 400 seconds. The determinant value is the concentration of disinfectant in water.
Response time

The response time is defined as the “time interval between the instant when the on-line sensor/analyser equipment is subjected to an abrupt change in determinant value and the instant when the readings cross the limits of (and remain inside) a band defined by 90 % and 110 % of the difference between the initial and final value of abrupt change” (2).

The positive response time is the time taken for an analyser to read 90% of the adjusted residual concentration after subjecting it to an increase in residual concentration. The negative response time is the time taken for an analyser to read 10% of the adjusted residual concentration after subjecting it to a decrease in residual concentration.

Using the example in Figure 3.53, the disinfectant concentration measured by the analyser prior to an increase of disinfectant concentration was \( y_{\min} = 1.0 \, \text{mg/L} \). At time \( t_{\min} = 0 \, \text{sec} \), the disinfectant concentration was abruptly increased from 1 to 2 mg/L. Time was taken for the analyser reading to stabilise at a maximum value of \( y_{\max} = 2.0 \, \text{mg/L} \). The time \( t_{90\%+} \) when the disinfectant concentration measured by the analyser is equivalent to 90% of the total abrupt change in disinfectant concentration (1.9 mg/L), is determined from recorded data (this is equivalent to 140 seconds). The response time, according to ISO 15839 (2), is then determined as:

\[
t_{\text{response}+} = t_{90\%+} - t_{\min}
\]

So, \( t_{\text{response}+} = 140 - 0 = 140 \, \text{sec} \).

Subscript plus refers to the case when the disinfectant concentration in water has increased. Response time for decrease of disinfectant concentration is determined similarly.

\[
t_{\text{response}-} = t_{10\%+} - t_{\max}
\]

So, \( t_{\text{response}-} = 340 - 200 = 140 \, \text{sec} \).
Delay time
The delay time is defined as the “time interval between the instant when the on-line sensor/equipment is subjected to an abrupt change in determination value and the instant when the readings pass (and remain beyond) 10% of the difference between the initial and final value of the abrupt change” (ISO 2003).

Using the example shown in Figure 3.23, the time when the analyser readings reached 10% of the total abrupt change in disinfectant concentration \( (y_{10\%} = 1.1 \text{ mg/L}) \) is \( t_{10\%} = 60 \text{ sec} \). Then, according to ISO 15839 (ISO 2003), the delay time is determined as:

\[
t_{\text{delay}+} = t_{10\%} - t_{\text{min}}
\]

So,
\[
t_{\text{delay}+} = 60 - 0 = 60 \text{ sec}.
\]

The delay time for a decrease of disinfectant concentration can be determined similarly.

\[
t_{\text{delay}-} = t_{90\%} - t_{\text{max}}
\]

So,
\[
t_{\text{delay}-} = 260 - 200 = 60 \text{ sec}.
\]

Rise and fall times
The rise time is defined as the “difference between response time and the delay time when the abrupt change in determinant value is positive” (ISO 2003).

\[
t_{\text{rise}} = t_{\text{response}+} - t_{\text{delay}+}
\]

So,
\[
t_{\text{rise}} = 140 - 60 = 80 \text{ sec}.
\]

Similarly, the fall time is defined as the “difference between response time and the delay time when the abrupt change in determinant value is negative” (ISO 2003).

\[
t_{\text{fall}} = t_{\text{response}-} - t_{\text{delay}-}
\]

So, \( t_{\text{fall}} = 140 - 60 = 80 \text{ sec}. \)

In the above examples the rise and fall time values were equal but in reality, they can vary significantly.

5.4.2 Linearity
Linearity is defined as the “condition in which measurements made on calibration solutions having determinant values spanning the stated range of the on-line sensor/analysing equipment have a straight line relationship with the calibration solution determinant values” (ISO 2003).

In other words, this performance indicator determines how closely the analyser readings match the results of titration tests on the test solution. The test for linearity can be determined by “graphical representation of the calibration data with the calculated regression line” (ISO 1990). Figure 54 presents arbitrary data that make understanding of linearity concept easier.
All data are plotted as $y_{reading} = f(y_{calibr})$, where $y_{reading}$ is the disinfectant concentration reading from an analyser, and $y_{calibr}$ is the disinfectant concentration in the test solution from laboratory analysis. Solid circles represent the ideal case, when analyser readings exactly match those from titration tests. This curve is inclined by 45° and represents a straight line. Case-1 and case-2 are represented by solid triangles and diamonds, respectively. Even from visual observation, it is clear that data from case-1 are closer to the straight line than those from case-2. However, this is a qualitative comparison only. ISO 8466-1:1990 (ISO 1990) states, that it is necessary to make conclusions using statistical methods of analysis. For this reason, these data were subjected to linear regression tests with the choice of the best fitting of the linear equation to the experimental data using mean-least squares approximation. The criterion for the best fitting is the value of the regression coefficient, $R^2$. The closer this coefficient is to unity, the closer the data are to the straight line. The values of these coefficients for the above two cases are: $R^2_{case-1} = 0.9928$ and $R^2_{case-2} = 0.9692$. The performance of the analyser for case-1 is better, and its $y_{reading} = f(y_{calibr})$ relationship is closer to the straight line.

### 5.4.3 Coefficient of variation

The coefficient of variation (COV) is defined as the “ratio of the standard deviation of the on-line sensor/analysing equipment to the mean of the working range of the equipment” (ISO 2003). The COV value can be used to compare the variation of different analysers. The COV combines the value for the regression coefficient ($R^2$) and the slope of the linearity test in one parameter, expressed in percent variation of the analyser measuring range.

In order to explain the definition of COV, consider results of 7 measurements over the working range of an analyser shown in Table 3.62.
The mean value of these measurements is determined as follows:

\[ y_{\text{mean}} = \frac{\sum_{i=1}^{n} y_{i,n}}{n} \]  

(7)

**Table 3.62** Example to calculate the COV

<table>
<thead>
<tr>
<th>Number of Measurement</th>
<th>Reference Value, ( x_i ) mg/L</th>
<th>Analyser Measurement, ( y_i ), mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>2</td>
<td>0.21</td>
<td>0.24</td>
</tr>
<tr>
<td>3</td>
<td>0.36</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>0.49</td>
<td>0.51</td>
</tr>
<tr>
<td>5</td>
<td>0.65</td>
<td>0.68</td>
</tr>
<tr>
<td>6</td>
<td>0.72</td>
<td>0.75</td>
</tr>
<tr>
<td>7</td>
<td>0.91</td>
<td>0.98</td>
</tr>
</tbody>
</table>

So,

\[ y_{\text{mean}} = \frac{0.09 + \cdots + 0.987}{7} = 0.5214 \text{ mg/L}. \]

The mean value of the working range of the equipment is calculated similarly:

\[ x_{\text{mean}} = \frac{0.11 + \cdots + 0.91}{7} = 0.4929 \text{ mg/L}. \]

The slope of linear regression, \( b \), as a measure of sensitivity, and is calculated from Equation (8):

\[ b = \frac{\sum_{i=1}^{n} (x_i - x_{\text{mean}})(y_i - y_{\text{mean}})}{\sum_{i=1}^{n} (x_i - x_{\text{mean}})^2} \]  

(8)

So,

\[ b = \frac{(-0.3829)x(-0.4314) + \cdots + 0.171 x \times 0.4586}{(-0.3829)^2 + \cdots + 0.4171^2} = 1.0698. \]

The ordinate intercept, \( a \), is calculated from equation (9):

\[ a = y_{\text{mean}} - bx_{\text{mean}} \]  

(9)

So,

\[ a = 0.5114 - 1.0698 \times 0.4929 = -0.0058. \]
The residual standard deviation $s_y$ is calculated as follows

$$
s = \sqrt{\frac{\sum_{i=1}^{n}(y_i - \bar{y})^2}{n-2}} = \sqrt{\frac{\sum_{i=1}^{n}(y_i - (a+bx_i))^2}{n-2}} \quad (10)
$$

where, $\bar{y}_i = a + bx_i$ is the value of the reference concentration, $x_i$, calculated using coefficients $a$ and $b$ obtained from equations (8) and (9).

So,

$$
s = \sqrt{\frac{(0.09-0.11)^2 + ... + (0.98-0.97)^2}{7-2}} = 0.0194.
$$

The standard deviation of the method $s_{x_0}$ is calculated as follows:

$$
s_{x_0} = \frac{s_y}{b} = \frac{0.0194}{1.0698} = 0.0181 \quad (11)
$$

The COV, expressed in percentage, can be calculated by equation 12:

$$
COV = \frac{s_{x_0}}{x_{mean}} \cdot 100\% \quad (12)
$$

So,

$$
COV = \frac{0.0181}{0.4929} \cdot 100 = 3.67\%.
$$

The smaller the COV the closer the analyser performs measurements to the reference measurement.

### 5.4.4 Limit of detection

The limit of detection (LOD) is defined as the “lowest value, significantly greater than zero, of a determinant that can be detected” (ISO 2003). In other words, LOD is related to the ability of the analyser to measure/detect the lowest value of disinfectant concentration in water that is greater than zero. Therefore, the analysers were exposed to a 5% test solution. According to the standard (2), LOD is calculated as three times the standard deviation.

As an example, an analyser responded 5 times to the lowest values of disinfectant concentration in water as follows: $0.01, 0.00, 0.01, 0.00, 0.01$ mg/L. According to Equation 7, the mean of these values is:

$$
y = \frac{0.01+0.00+0.01+0.00+0.01}{5} = 0.006 \text{ mg/L}.
$$

The standard deviation of the values can be calculated with equation (13):
So, LOD = 3 x 0.0055 = 0.0165 mg/L.

The smaller the value of LOD, the smaller disinfectant concentration an analyser can detect.

5.4.5 Limit of quantification

The limit of quantification (LOQ) is defined as the “lowest value of determinant that can be determined with an acceptable level of accuracy and precision” (ISO 2003). The LOQ is equal to 10 times the standard deviation (ISO 2003). This indicator can be evaluated from measurements of very low disinfectant concentration solutions within the accuracy and precision claimed by the manufacturer for each analyser. Therefore, the analysers were exposed to a 5% test solution.

Using the data presented in the LOD example, LOQ is calculated as follows:

\[
\text{LOQ} = 10 \cdot \text{LOD} \tag{15}
\]

So, LOQ = 10 x 0.0055 = 0.055 mg/L.

Therefore, \( \text{LOQ} > \text{LOD} \).

The LOQ is bigger than the LOD, which does not account for the accuracy and precision of the analyser.

As an example, the local Environment Protection Authority (EPA) restricts the chlorine concentration in the discharged water to 0.005 mg/L. An analyser has delivered the following readings: 0.001, 0.005, 0.003, 0.001, 0.002 mg/L. According to equation (7) and (12), the mean value and the standard deviation of the values are as follows:

\[
\text{mean} = 0.0024 \text{ mg/L, and } \text{stddev} = 0.00167 \text{ mg/L.}
\]

The LOD and LOQ according to Equations (13) and (14) are:

\[
\text{LOD} = 3 \times \text{stddev} = 3 \times 0.00167 = 0.005 \text{ mg/L}
\]

\[
\text{LOQ} = 10 \times \text{stddev} = 10 \times 0.00167 = 0.167 = 0.017 \text{ mg/L.}
\]

Therefore, the lowest value of chlorine concentration that can be determined by the analyser with acceptable level of accuracy and precision is 0.017 mg/L. This makes it unsuitable for EPA environmental discharge applications where the required LOQ is 0.005.
5.4.6 Repeatability and day-to-day repeatability

Repeatability and day-to-day repeatability are defined as “precision under repeatability and precision under day-to-day repeatability conditions” (ISO 2003). The repeatability and day-to-day repeatability conditions are defined as “conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment and reagents within short intervals of time (e.g. one day for repeatability) or over several days (for day-to-day repeatability)” (ISO 2003), respectively.

Repeatability is determined for the both test solutions, 80% and 20% of the analyser working range. Chlorine analysers with the working range from 0 to 2 mg/L correspond to chlorine concentrations of 0.4 and 1.6 mg/L and ammonia analysers with a working range from 0 to 1 mg/L correspond to 0.2 and 0.8 mg/L, respectively. Repeatability is calculated as the standard deviation of measurements.

As an example, consider arbitrary responses from an analyser for a nominal 80 % solution equivalent to a concentration of 1.60 mg/L. The analyser has supplied the following data: 1.62, 1.66, 1.61, 1.68, and 1.64 mg/L. The repeatability, $R$, is equal to the standard deviation according to Equation (9).

$$y_{\text{mean}} = 1.642 \text{ mg/L, and } y_{\text{stddev}} = 0.0286 \text{ mg/L.}$$

$$R = y_{\text{stddev}}$$

So,

$$R = 0.0286 = 0.03 \text{ mg/L.}$$

The repeatability at 80% of the working range is 0.03 mg/L for this analyser.

Day-to-day repeatability is determined similar to repeatability, and is reported for the upper half, 65%, and the lower half, 35% of the analyser working range, which for a chlorine analyser corresponds to chlorine concentrations of 1.30 and 0.70 mg/L and for an ammonia analyser to ammonia concentrations of 0.65 mg/L and 0.35 mg/L, respectively, during this trials.

5.4.7 Lowest detectable change

Lowest detectable change (LDC) is defined as the “smallest significantly measurable difference between two measurements” (ISO 2003). It is calculated as three times the standard deviation of measurements made at 20 and 80% of the analyser range.

Using the data supplied in the example from section 8.2.10, the mean value and the standard deviation are:

$$y_{\text{mean}} = 1.642 \text{ mg/L, and } y_{\text{stddev}} = 0.0286 \text{ mg/L.}$$

The LDC is three times the standard deviation:

$$\text{LDC} = 3 \times y_{\text{stddev}}$$

So, $\text{LDC} = 3 \times 0.0286 = 0.086 \text{ mg/L.}$

The calculation for LDC is similar that used to calculate LOQ except that measurement is carried using a 20 and 80% solution instead of a 5% solution which was used for the LOQ test.

5.4.8 Bias

Bias is defined as the “consistent deviation of the measured value from an accepted reference value” (ISO 2003). This indicator is determined by the comparison of analyser readings with titration results for the testing solutions and is usually expressed in the units of the concentration. In Figure 3.55, solid circles represent ideal case when analyser readings exactly match those of laboratory analysis results.
Closed triangles represent an analyser’s arbitrary test results. It can be seen that the analyser readings are systematically above the corresponding laboratory results by 0.1 mg/L. This means that analyser readings are biased. In other words, a systematic error is introduced into the measurements. To use the correct analyser readings, the value of 0.1 mg/L should be subtracted from the readings.

![Figure 3.55 Arbitrary results for bias test.](image)

### 5.4.9 Short-term drift

Results produced by analysers may drift under constant testing conditions in the middle of a measuring range. Such behaviour is described by a short-term drift (ShTD) characteristic. This is defined as the "slope of the regression line derived from a series of measurements carried out on the same calibration solution during laboratory testing, and expressed as a percentage of the measurement range over 24 h period" (ISO 2003).

Arbitrary results from a ShTD test carried out over a period of 24 hours are shown in Figure 3.26. Solid circles represent laboratory analysis results and the standard deviation of this data is 0.02 mg/L. This result falls within the experimental uncertainty of the analyser. Experimental data obtained from the analyser readings are shown as closed triangles. A declining trend over 24 hour period is observed in Figure 3.56 for analyser readings. If a regression line is drawn through triangles, the following equation will describe the straight line:

\[
y_{str.line} = -0.0074x + 1/6399.
\]

Here, x is time in hours. According to the definition, a ShTD can be expressed as follows:

\[
ShTD = \frac{slope \cdot 100\%}{range_{max} - range_{min}}
\]

(18)

\[
ShTD = -\frac{1.0074 \cdot 100\%}{2} = -0.37\%.
\]

So,
Values in the denominator are maximum and minimum measuring ranges for the analysers. The smaller the ShTD value, the less analyser readings are tending to drift with time. Ideally, ShTD value should be within the experimental uncertainty of the analyser.

### 5.4.10 Memory effect

The memory effect is a “temporary or permanent dependence of readings on one or several previous values of the determinant. The memory in online sensor/equipment is typically observed as a saturation effect caused by the fact that a determinant value is well above the working range of the equipment. Memory effect can either be temporary or permanent, but in both cases the fall time after equipment has experienced a peak determinant value above its working range will be increased. If the memory effect is a permanent one, it will typically introduce a positive offset in the equipment (ISO 2003).

A memory effect test consists of exposing an analyser to a test solution with a determinant value of 200% of the working range and then changing the sample to a 20% test solution. This cycle is then repeated six times. The memory effect is reported as the difference between the mean value of the six measurements of the 20% test solution and the determinant value (reference measurements) (ISO 2003). The analyser is said to have a memory effect if the calculated value is bigger than the result of the LDC on a 20% test solution (LDC_{20%}) (ISO 2003).

Figure 3.53 shows the response of an analyser (analysers a) to the variation of disinfectant concentration in water. The working range for this analyser is 0 to 2 mg/L. The fall and negative delay time without memory effect were:

\[
\begin{align*}
    t_{\text{delay}} &= - - - - - - , \\
    t_{\text{fall}} &= - - - - - .
\end{align*}
\]

Figure 3.57 shows an arbitrary response of a different analyser (analyser b) with a memory effect (open triangles). The data from the analyser a is shown in Figure 3.27 as closed circles and it can be seen that the disinfectant concentration in the water starts to increase from 1 to 3 mg/L and stays there for 200 seconds. After that, the concentration drops to 1 mg/L. Analyser b shows the same performance during the increase in disinfectant residual concentration but is sluggish when the
change from high to low concentration occurs (Figure 3.57). The fall and negative delay time with memory effect can be evaluated as follows:

\[
\begin{align*}
\text{response}_{-} & = - - - - , \\
\text{delay}_{-} & = - - - - , \text{ and} \\
\text{fall}_{-} & = - - - - .
\end{align*}
\]

Negative delay time and fall time will increase if an analyser shows a memory effect. The permanent memory effect can be seen, introduced as positive zero offset (0.1 mg/L) in the analyser readings.

### 5.4.11 Interferences

The performance of an online analyser is determined not only by the fact of how accurately it responds to disinfectant concentration variations in water, but also how insensitive it is to other interferences. The results from an online disinfectant residual analyser should not be influenced by changes that may occur to other water quality parameters such as temperature, pH, conductivity, etc. In some cases, analysers can develop “undesired output signal caused by a property(ies)/substance(s) other than the one being measured” (ISO 2003), which is called interference. This effect can be investigated by subjecting an analyser to changes in sample pH and electrolytic conductivity. For each of these interferences changes, the analyser readings in the percentage of its measuring span are determined.

As an example, two analysers (analyser 1 and analyser 2) were supplied with water from the same pipe. The measuring range of both analysers is 0 to 2 mg/L. The pH value of the water was controlled at pH 7. The disinfectant residual concentrations measured by these two analysers were as follows:

\[
y_{10} = \frac{y}{L} \text{ and } y_{20} = \frac{y}{L}.
\]
The actual disinfectant concentration from laboratory analysis is equal to

\[ y_{w0} = \frac{0.90}{\text{titr}} \text{ mg L}^{-1}. \]

Then, the pH of water was increased to \( pH = 8 \). After a period of time, the disinfectant residual concentration readings of these two analysers had stabilised showing the following values:

\[ y_{11} = \frac{0.99}{\text{titr}} \text{ mg L}^{-1} \quad \text{and} \quad y_{21} = \frac{0.95}{\text{titr}} \text{ mg L}^{-1}. \]

The actual disinfectant concentration from laboratory analysis is equal to

\[ y_{w0} = \frac{0.90}{\text{titr}} \text{ mg L}^{-1}. \]

The percent variation of the analysers measuring range for pH change, \( pH = 7 \rightarrow 8 \), can be calculated as follows with Equation 19:

\[
Interference_1 = \frac{y_{11} - y_{10}}{\text{range}_{\text{max}} - \text{range}_{\text{min}}} \times 100\%
\]

So, \( Interference_1 = \frac{0.99 - 0.89}{2} \times 100\% = 5\% \).

\[
Interference_2 = \frac{\text{range}_{\text{max}} - \text{range}_{\text{min}}}{\text{range}_{\text{max}} - \text{range}_{\text{min}}} \times 100\% = 0\%.
\]

Similarly,

The above results show, that the second on-line chlorine analyser is less sensitive to pH variation. This analyser should be preferred in applications with possibilities of pH changes in water.
1 INTRODUCTION

Natural computing sources inspiration from biological mechanisms and patterns of behaviour to develop novel computational algorithms for solving complex problems. Natural computing has been largely popularised through the application of artificial neural networks (ANNs) and evolutionary computing. The application of ANN techniques to water quality modelling has generated a great deal of interest among researchers and practitioners, which is evident from the number and diversity of reported applications in this field. The ability to analyse and develop models of complex, non-linear systems using these techniques makes them attractive for the study of many environmental systems, and they are increasingly being found to be superior to more conventional modelling and analysis tools. This is evident from the number of applications that can be found within the literature, which include:

- prediction and forecasting,
- process control,
- integrated modelling,
- metamodelling, and
- knowledge extraction.

Much of the popularity of ANNs is derived from their ability to perform a variety of complex modelling tasks such as prediction, classification and clustering. However, the same highly flexible and unstructured nature of ANN techniques that makes them so useful and appealing to modellers, also leads to uncertainty regarding their reliability, accuracy, and transparency. This dichotomy highlights the importance of developing an understanding of how ANN techniques can best be used to develop improved models, or further our understanding of environmental systems. To this end, there is a need for modellers to establish guidelines for the development and application of ANN tools that can increase the robustness and transparency, and therefore confidence and acceptance, of ANN modelling techniques as a modelling tool within the water resources field.

This chapter presents an overall framework for the development of ANN models that provides some guidance with respect to the decisions at each stage of ANN development. Section 2 provides some context for ANN model development, by briefly highlighting the different applications for which they have been found to be useful. Section 3 describes two widely used neural network architectures, for those less familiar with the workings of these models.
Finally, Section 4 discusses the components that form the overarching framework for ANN development, which include:

- data collection;
- data preprocessing;
- input variable selection;
- data subset selection;
- training (calibration);
- model selection, and
- model validation.

2 APPLICATIONS IN WATER QUALITY MODELLING

Based on the number of potential uses for ANN models within a wide variety of applications, it is evident that ANN model development is an attractive alternative. In most cases, the applications where ANNs demonstrate utility are not necessarily novel, and conventional modelling tools already exist. However, the ANN approach may offer either improved performance, or be easier to implement than other approaches. The main advantage of ANN techniques is that they can often be utilised when there is an abundance of data, but relatively poor understanding of the system under consideration, and they are therefore ideally suited to the “data-rich, knowledge-poor” circumstances often encountered by environmental modellers.

2.1 Prediction and forecasting

Modelling processes and forecasting of time series have been some of the predominant applications for artificial neural networks in all fields of science, engineering and mathematics. In this capacity, ANN architectures provide a powerful inference engine for both regression and classification. This stems from the ability of ANNs to map non-linear relationships, which is more difficult and less successful when using conventional time-series analysis or regression/classification tools, which are invariably derived from linear analysis. In this sense, the ANN approach is best thought of simply as a non-parametric form of regression, where the ANN provides a model of the form

\[ y = F(X) + \varepsilon \]  

where \( F \) is an estimate of some variable of interest, \( y \); \( X = X_1, \ldots, X_p \) denotes the set of input variables or predictors, and \( \varepsilon \) is a small noise or error term. The training of the ANN is analogous to parameter estimation in regression. However, the difference is that, using a single base architecture, the ANN can approximate any functional behaviour without the prerequisite a priori knowledge of the structure of the relationships that are described. Numerous applications of predictive ANN models to water resources modelling and time-series analysis have been reported. Some examples include forecasting of water quality parameters in surface waters, such as salinity [Maier and Dandy, 1998], biological oxygen demand (BOD), suspended sediment [Cigizoglu, 2004; Alp, 2007], and cyanobacteria concentrations [Bowden, 2003; Kingston, 2006; Lui and Li, 2007]. In hydrology, ANN models have been developed for rainfall-runoff modelling and streamflow forecasting [Dawson and Wilby, 2001; Lobbroche and Solomatine, 2002; Jain and Srinivasulu, 2006]. ANN applications in water supply management applications have included modelling of water and wastewater treatment processes [Baxter et al., 2000; El-Din et al., 2004; Maier et al., 2004; Raduly et al., 2007], forecasting of disinfectant residual [Serodes et al., 2001; Bowden et al., 2006; May et al., 2008b], and modelling the evolution of disinfection by-product (DBP) concentrations in water supply [Milot et al., 2002].

2.2 Process control

The development of advanced control systems using ANN models has received considerable attention. The ability of ANN models to provide an efficient transfer function for complex non-linear processes has been recognised as a major advantage in the development of control algorithms for applications where linear process identification fails and conventional non-linear identification becomes difficult. Another advantage of ANN approaches to controller development is their adaptive capability. Unlike conventional controllers, neural control systems can learn and adapt to subtle changes in the process. This is an inherent problem in model-based control, because invariably all control models are developed off-line using a sample of data, and poor controller performance results
when previously unseen conditions are encountered. The ability of control systems to self-adapt in such a way forms the basis for adaptive or intelligent control, and ensures that control system performance is maintained post deployment.

Model predictive control (MPC) and inverse model control (IMC) are two control types that have been applied within an environmental engineering context. The MPC approach utilises an ANN predictive model to optimise controllable inputs based on the predicted system response. This has been applied to control of the coagulation process within a water treatment plant [Baxter et al., 2000], and real-time control of stream flow [Lobbrecht and Solomatine, 2002]. In the IMC approach, an ANN is trained to predict the required value of one or more manipulated parameters to achieve a specified process output, incorporating changes in other process variables. This is more direct than MPC, since the ANN instantly predicts the correct control signals. This has been demonstrated for controlling coagulation within a water treatment process, where the correct alum dose is predicted for a set-point turbidity and variable raw water quality [Maier et al., 2004], and the optimal disinfectant dose is determined based on demand and water quality [Rodriguez and Serodes, 1999].

2.3 Integrated modelling

Rather than represent a process fully using a single model, the combination of ANN and conventional models is also a promising technique that leads to the development of integrated or hybrid models. In this case, the utility of ANN models has been to enhance the development of existing models, by providing a functional representation of one or more non-linear process components. Such application of ANN models has seen extensive use within environmental modelling applications, where it is not unusual for the scope of a modelling study to consider multiple interacting systems.

In the case where a given system component is understood very well, and an existing physical or conceptual model is available, the conceptual model is used for this component. However, the model may yet require additional inputs or information about state variables for less-understood system components, for which a conceptual model may not be available, and an ANN can be used to develop a model based on available data to represent the unknown process. Sometimes it may also be acknowledged that the best available physical model does not fully describe a system, owing to some unknown process, which results in a structured error in model estimates. This forms the motivation for data fusion, which uses the available data to develop ANNs that can predict, and therefore compensate for, the error in the conceptual model, or improve predictions by combining outputs of one or more models that each partially describe a system [See, 2008].

Regardless of the approach taken, the acceptance of ANN techniques in integrated model development presents a more mature understanding of the limitations of both conventional models and ANN techniques. Previously, researchers focussed on pitting modelling techniques against each other. However, there is now an increasingly recognised mutual benefit for obtaining more accurate models by combining the two approaches to exploit their respective strengths [Jain and Srinivasulu, 2006].

2.4 Metamodelling

The efficient representation of complex systems using ANN techniques has also been exploited in applications requiring multiple instances of computationally expensive simulations, such as Monte Carlo simulation and optimisation. Broad et al. [2005] used an ANN to represent a simulation of a water distribution system to implement an efficient genetic algorithm optimisation of pipe sizes based on hydraulic and water quality objectives. Similarly, Raduly et al. [2007] utilised an ANN metamodel to represent a simulation of a wastewater treatment process for controller development.

In this approach, an ANN is trained to predict the input-output behaviour of an existing simulation or model of a process. Once the ANN metamodel has been developed, it takes the place of the conventional model during subsequent analyses. Here, the benefit is to reduce the overall computational effort, since the ANN can generate a faster input-output response than the conventional model. A typical analysis could require in the order of $10^5–10^6$ simulations, so a reduction in the computation per instance offers an immense potential to reduce, by a significant amount, the total time required for the overall analysis.
2.5 Knowledge extraction

Knowledge extraction is concerned with the extraction of information based on the analysis of a trained ANN to determine the relative strength of input-output relationships, or causal interactions between different system variables. Techniques for knowledge extraction include sensitivity analysis and importance analysis [Andrews et al., 1995]. In each case, the approach is to take a trained ANN and review the strength of input-output connections. Strong connections or a high degree of sensitivity tend to suggest important relationships between variables. Correlation structure within the connection weights also implies relationships between input variables that are not always immediately apparent by examining the input data.

Knowledge extraction can be a useful diagnostic tool, since confirmation that the network architecture has correctly identified known relationships can increase confidence in the ANN [Kingston et al., 2006b]. Alternatively, the ANN can be interrogated to determine previously unknown relationships and help to form a novel conceptual model [Wilby et al., 2003; Jain et al., 2004].

3 NEURAL ARCHITECTURES

Architectures that feature prominently within ANN water quality modelling and analysis applications are: the multilayer perceptron (MLP), and the generalised regression neural network (GRNN).

3.1 Multilayer perceptron

The multi-layer perceptron is the quintessential ANN architecture. The MLP is by far the most popular of all ANN architectures, and its use is reported in approximately 90% of applications using ANNs. The classic three-layered MLP, shown in Figure 4.1, comprises three layers of neurons representing the input and output, with a single hidden layer. Each layer is fully connected to the subsequent layer by a hyperplane of connection weights.

![Figure 4.1 Architecture of the classic 3-layered multilayered perceptron (MLP), which comprises three layers of neurons representing the input and output, with a single hidden layer. Each layer is fully connected to the subsequent layer by a hyperplane of connection weights.](image-url)
The $p$ input layer nodes denote the individual component variables, $x_i$, of the $p$-dimensional input vector. Each variable is then connected by a connection weight $v_{ij}$ to each neuron in the hidden (middle) layer (so called because the activation of nodes in the middle layer is generally not observed). The weighted input variables are summed to form the input activation signal $z_j$, which is then transformed to the hidden node output according to the hidden-node transfer function, $f(z_j)$. The outputs from each hidden node are connected to one or more output nodes that denote the variables, $y_k$, by a second hyperplane of connection weights, denoted as $w_{jk}$. An additional bias node (0) in the hidden layer has a constant unit output, which adds a bias to each output according to its corresponding connection weights.

The transfer function for nodes in the hidden layer could theoretically be any function, although in the case of the MLP typically four are used: linear gain, step function, sigmoidal and hyperbolic tangent, as given below by Equations. 2, 3, 4 and 5, respectively.

\[
f(z) = z \quad (2)
\]
\[
f(z) = 1 \text{ if } z > 0, \text{ otherwise } 0 \quad (3)
\]
\[
f(z) = \frac{1}{1 + e^z} \quad (4)
\]
\[
f(z) = \tanh(z) \quad (5)
\]

In order to achieve non-linear mapping, the non-linear (sigmoidal, hyperbolic tangent) transfer functions need to be specified. The step function is typically used in the output node for classification applications that require a binary response.

### 3.2 Generalised regression neural network

The generalised regression neural network (GRNN) was developed by Specht [1991], and represents an ANN paradigm for kernel regression. The architecture of the GRNN, shown in Figure 4.2, comprises four layers. The first and last layers represent the input and output vector. The second (pattern) layer represents $n$ training observations of $(x, y)$. The two nodes in the summation layer represent the numerator (num) and the denominator (den) in the kernel estimation of the conditional expectation $E(y|x)$.

The flow of data through a GRNN begins by presenting a sample $x$ to the network, which defines the input signals from each node to the pattern layer. At each pattern layer node $j$ the activation $a_j(x)$ is determined based on a kernel function centred on training input vector $z_j$. The Gaussian kernel function, in which the Euclidean distance metric determines the activation, is typically used as the activation function in the pattern layer. In this case the activation is given as

\[
a_j(x) = e^{-|x-z_j|^2 / 2h^2} \quad (6)
\]

where $h$ is the GRNN bandwidth, or smoothing parameter. Specht [1991] observes that the more efficient Manhattan (or city block) kernel is also a suitable choice of function. However, within literature on kernel regression, setting the correct value of the bandwidth is considered to be more important for obtaining accurate predictions than the choice of kernel [Scott, 1992].

The activation of each pattern layer node is passed to the two nodes in the summation layer, which each generates weighted sums of the pattern node activations.
Figure 4.2 Architecture of the general regression neural network (GRNN), which comprises four layers. The first and last layers represent the input and output vector. The second (pattern) layer represents \( n \) training observations of \((x,y)\). The two nodes in the summation layer represent the numerator \((\text{num})\) and the denominator \((\text{den})\) in the kernel estimation of the conditional expectation \(E(y|x)\).

The connection weights between the \textit{num} summation node and the pattern layer are the values \(y_j\) that correspond to each \(z_j\), so that the activation of the \textit{num} summation node is given as

\[
\text{num} = \sum_{j=1}^{n} y_j a_j
\]  

(7)

The connection weights between to the \textit{den} summation node are equal to 1, and the activation at this node is given as

\[
\text{den} = \sum_{j=1}^{n} a_j
\]  

(8)

In the output layer, the ratio of the activations of the \textit{num} and \textit{den} nodes determines the network output, so that the overall GRNN function can be written as

\[
y = \frac{\sum_{j=1}^{n} y_j a_j}{\sum_{j=1}^{n} a_j}
\]  

(9)

which is simply the kernel estimate for the conditional expectation, \(E(y|x)\), that is, the conditional expectation of \(y\) given \(x\).
It is also worth noting that the GRNN is essentially a special case of the more general radial basis function (RBF) network. An RBF network specifies a set of basis functions $f_j$ of width $h_j$. However, the RBFs are positioned at centres $c_j$ rather than at training points $z_j$ and the function outputs are weighted by weights $w_j$. In an RBF network, each of these parameters are initially random, and then optimised during training.

4 MODEL DEVELOPMENT

How to best proceed with the development of an ANN for a given application can be daunting for modellers, since the ANN framework is inherently very flexible and the modeller is faced with many decisions during development. As much as 90% of the effort associated with the implementation an ANN application is focused on the initial model development. The overall steps during ANN development, and the modelling decisions required at each stage, are illustrated in Figure 4.3. In many applications, the focus of ANN development is on the architecture and the learning algorithm. However, before, during and after the training of an ANN, there a number of considerations, that are arguably more influential on model performance.

4.1 Data collection

The first step in the development of ANN models (indeed, of any model) is to collect some data that are representative of the behaviour of the system under consideration. This requires that the model development objectives be clearly defined from the outset, as these will most likely form the basis for data collection, in terms of identifying and monitoring the variables of interest (the outputs) and potential explanatory variables (input variables). Once the modelling objectives and variables are defined, the commonly asked question is: How much data should be collected? Ultimately, this will usually depend on various considerations, some of which may not necessarily be related to the requirements of ANN training, but be more pragmatic considerations.

4.1.1 Observability

Observability is the extent to which it is possible to gain insight into the behaviour of a system through observation. The observability of systems has major implications for the development of ANN models, which are inherently dependent on obtaining a dataset that describes the behaviour to be learnt during training. Limited observability often results from an inability to measure parameters, which must then be inferred by another measurable parameter, or remain an unknown process. The variability of a system during the data collection period should be considered, since it is desirable for the dataset to contain representative data of all extremes of system behaviour. It may be the case that the system does not exhibit wide variation, and remains stable about a steady-state operating condition, which makes it fundamentally very difficult to establish an inference of input-output responses or system dynamics. This will often be the case in systems that are stable (or at least changing at an unnoticeable rate) or are under tight operational control. If it is possible to manipulate the process in a controlled manner, then it is worth considering undertaking some experiments to induce variation, in order to generate a representative set of data. This kind of experimentation is often performed during system identification of process plants. In more natural systems, this is less likely to be possible, and limited observability will therefore pose a constraint for model development.

4.1.2 Seasonality

Many natural processes are cyclic, with periodic fluctuations from one extreme state to another. This is referred to as seasonality, since the most common example is time series that show cyclic behaviour due to transitions between Summer (warm) and Winter (cold) seasons over the course of a year. However, seasonality is not limited to annual cycles, but refers to any period of oscillation within a system, such as tidal fluctuations in coastal zones, or diurnal and weekly cycles in demand for power and water. The important consideration is that the collection of data is able to capture an entire cycle, or preferably several cycles. Doing so ensures that the ANN is trained with data that are representative of all extremes of system behaviour. Using less than a full cycle would most likely bias the model development towards the particular season (or part thereof) during which data were collected. For example, in water supply systems, the timing of daily grab sampling may bias the data owing to to the diurnal profile of demand within the system. In this case, samples taken early in the morning, coinciding with a period of low flow, would be expected to yield a low disinfectant residual,
whereas samples taken shortly after peak demand would have an elevated disinfectant residual. Consequently, on-line monitoring (or a composite sample) would be recommended to capture (or aggregate) the fluctuations in water quality over the course of a 24-hour period.

Figure 4.3 Framework for the development of ANN models, from data collection to model deployment.
4.1.3 Cost

Obtaining data is expensive, and it is unlikely that the modeller will be provided with an infinite budget. Consequently, there is a trade-off between the amount of data collection that is required, and what can be afforded within the scope of a given project budget. Choosing to utilise variables that are already routinely monitored is perhaps the best way of reducing the cost of model development. Most modellers will source data from the process SCADA (supervisory control and data acquisition) or databases of monitoring that is undertaken by various agencies working within the environmental system under consideration. Where data are to be collected specifically for model development, the duration and scope of experimentation can be optimised to ensure that the amount of data collected can encompass the previous considerations of seasonality and observability. Given the choice of two variables, if more frequent measurements of one variable could be made with a slightly less accurate technique, this variable might yield more informative patterns.

Environmental systems are often large scale, which can add to the cost of monitoring. Modellers should also consider making use of inexpensive modern communications hardware and software, such as robust field data loggers and mobile (IP) networks to ensure cost-effective data collection. These are becoming increasingly affordable and easier to use, with minimal expertise in instrumentation required.

4.2 Data preprocessing

The range and distribution of data can have a significant impact on the results of data analysis, since many algorithms are developed based on some underlying assumptions regarding the range and distribution of the data. Data that fail to meet these assumed criteria can lead to unexpected and undesirable results. In the second stage of model development, pre-processing of the raw data aims to ensure that the data are appropriately distributed for the analysis that is to be undertaken.

4.2.1 Linear scaling

Linear scaling of data is a common pre-processing step that is required for many data analysis techniques, including regression and ANN modelling. Datasets usually contain a variety of measurements reflecting a range of engineering units, and consequently the magnitude of absolute values can vary significantly for different variables. A linear scaling transformation onto the interval \([a,b]\) is given as

\[
x \rightarrow (b - a) \left( \frac{x - \text{min}}{\text{max} - \text{min}} \right) + a
\]

Another reason for linear scaling of the data range is to ensure that data analysis is effective, since algorithms may assume a specified range. The most common example of this is in the development of the MLP. The logistic and hyperbolic tangent functions used to define the activation of neurons in the hidden layer of the MLP are prone to saturation if the total input signal to the neuron is sufficiently high, or low. For a sufficiently large (positive or negative) value of \(z_i f(z) \rightarrow 0\). The result is that perturbations of \(w_{ij}\) within this domain achieve little no change in the output of the model. During training, this phenomenon slows learning or can result in early termination, since the error function will not change, leading to the development of a sub-optimal model. Best results are generally obtained when the input variables are linearly scaled to avoid saturation of the hidden-layer neurons. It is often recommended that the data are scaled to lie within 10–95% of the sensitive domain of the transfer function.
4.2.2 Standardisation

Standardisation is another transformation that is utilised for data pre-processing, where data are converted to normalised Z-scores, where data represent deviations rather than absolute values. The standardisation transformation is given as:

\[ x' = \frac{x - \mu}{\sigma} \]  

(11)

where \( \mu \) is the sample mean, and \( \sigma \) is the sample standard deviation. Standardisation transforms the data to have unit standard deviation, and a zero mean.

4.2.3 Logarithmic transformation

Some variables do not vary linearly over their ranges, and instead may change in orders of magnitude. In this case, it is common to use a logarithmic transformation of these variables to linearise the ranging of the variable. The logarithmic transformation is given as

\[ x' = \log_e x \]  

(12)

4.2.4 Lagging and leading

Models of dynamic processes are often constructed around a regressor, which simply refers to a window of past observations of input variables. The set of input variables may include past (delayed, or lagged) observations of the output variable, which are called endogenous lags; or other input variables (exogenous lags) that may influence the behaviour of the output variable. Given a time series \( x_t \), the lagging transformation is simply the shift operator

\[ x' = x(t - d) \]  

(13)

where \( d \) is the delay in time-steps. Similarly, in forecasting applications, the target output series \( y(t + h) \) is generated from \( y(t) \), where \( h \) is the forecasting horizon. Since lags cannot be generated for the first \( d \) variables, and forecast targets cannot be generated for the last \( h \) variables, the length of the transformed dataset will be reduced to \( n - d - h \) observations.

4.2.5 Pre-whitening

Many time-series applications deal with seasonal or periodic systems; this is observed as autocorrelation within the time-series data. Pre-whitening is a commonly employed preprocessing step in the development of statistical models of dynamic processes, where data are assumed to be stationary [Box and Jenkins, 1976]. While pre-whitening is not strictly a requirement for ANN learning [Maier and Dandy, 1997], strong correlations due to seasonality are often uninteresting and can dominate over other causal relationships within the data, and it may be useful to pre-whiten the data. The pre-whitening transformation is given as

\[ x_t' = x_t - F(x) \]  

(14)

which essentially determines the residuals based on the construction of a filter \( F \) that generates seasonal estimates of \( x \). A common example is seasonally adjusted rainfall or temperature data, which are filtered by subtracting the long-term seasonal average.

4.3 Input variable selection

The task of input variable selection (IVS) forms the third step the development of an ANN model, following from data collection and pre-processing. This step is common to all statistical modelling techniques where there are essentially no constraints on what variables could be used, but it is desirable to determine which ones should be used. The importance of the IVS task is evident when considering the issues surrounding selecting either too few, or too many, input variables, which are summarised as follows:
Information. Model accuracy will be poor if too few or insufficiently relevant variables are selected, since the ANN will lack sufficient information to predict the behaviour of the output variable.

Computational Effort. The obvious effect of a greater number of variables is a larger ANN, which can increase the computation burden associated with training and querying the network, especially in MLPs, where the increase in network parameters is multiplied by the number of hidden nodes for each additional input variable. Processing times for other computational analyses during model development are also increased.

Training Difficulty. The inclusion of irrelevant or redundant variables makes the task of training an ANN more difficult. The effect of redundant variables is to increase the number of local optima in the error function, which increases the risk of sub-optimal convergence. The increased complexity of the error function also slows the learning process. Irrelevant variables further increase the noisiness of the data and the complexity of the model, but yield no additional information regarding the behaviour of the output variable.

Dimensionality. The so-called "curse of dimensionality" is that, as the dimensionality of a model increases, the size of the input domain increases exponentially. Hence, from a statistical perspective, as dimensionality increases, an exponentially increasing number of samples is required to maintain an equivalent accuracy of the mapping. Since modellers will generally have a finite amount of data, the confidence in model accuracy will diminish accordingly for models of increasing dimensionality.

Interpretability. Minimising the complexity of the network is beneficial for knowledge or rule extraction, since the connections within simpler models are easier to interpret. Larger ANNs, and particularly those with redundant input variables, can achieve an accurate input-output mapping, but will often yield surprising or nonsensical relationships, which reduces confidence in the validity of the model.

Figure 4.4 illustrates the IVS problem, by considering the development of an ANN for one-step-ahead prediction of time-series \( Y(t) \), which is potentially dependent on exogenous variables \( X_1, X_2 \) and \( X_3 \). Here, it is considered that the dynamics of the system described by these variables shows persistence up to \( t - 4 \), and so the potential set of variables includes all endogenous and exogenous lags that fall within this window.

The common approach to ANN development is to simply include all lagged variables, regardless of whether all of these variables are absolutely necessary. This is because the ANN, when presented with some training data, will learn the important relationships and simply ignore any non-existent relationships. Given the uncertainty regarding whether or not a potential input should be included, many modellers will simply include all of them, and defer the task of identifying the relevant variables to the training step. However, this is a common misconception, which tends to ignore the negative issues caused by a large input variable set. A better approach is to determine an optimal subset of inputs, as shown on the right in Figure 4.4. As can be seen in this illustrative example, one input variable is determined to be irrelevant, and some lags are identified as being redundant, resulting in a more parsimonious set of input variables, without information loss.

Numerous different approaches for selecting input variables for neural networks have been described within the literature, although methods can be generally be classified as either wrappers or filters [May et al., 2008a]. These two approaches are illustrated in Figure 4.5. The important characteristic of any IVS strategy is its ability to identify relevant variables, and redundant ones, with robustness and efficiency.
4.3.1 Wrappers

Wrapper selection is based on the iterative evaluation of models using different subsets of input variables, and selection of the subset that corresponds to the best performing model. Wrapper algorithms vary according to how they search through the many combinations of input variables. Forward selection begins with one input, and adds inputs in succession. Conversely, backward elimination starts with all candidates and iteratively eliminates irrelevant or redundant variables. Wrapper selection is also easily embedded within evolutionary ANN development, where the inclusion or exclusion of variables form the binary decision variables within the optimisation of the ANN architecture.

The main benefit of the wrapper approach is that it guarantees that model performance is optimised, with respect to the choice of input variables. However, training and testing a potentially large number of networks requires a great deal of computational effort, and wrapper algorithms can be computationally expensive. Furthermore, the selections obtained for a given combination of architecture, learning algorithm and performance measure, cannot be strictly assumed to be optimal for another combination. Finally, the wrapper approach is often criticised since the tendency for large ANN architectures to overfit data can favour the selection of a large number of input variables.

4.3.2 Filters

Filters are a model-free approach to IVS, where some measure of dependence is used to determine whether or not each candidate variable should be included in the set of input variables. Since filters avoid the need to train and test many networks, they can implement selection significantly faster than wrapper algorithms. It is also considered that the separation of IVS from the choice of architecture provides an additional benefit, since the selections are not tied to a particular ANN architecture.
Correlation ranking is a common filter approach, in which the top-ranking \( p \) input variables are selected based on linear correlation with the output variable. Such a ranking approach is rather simplistic, and takes into account only relevance, but ignores redundancy and synergism between variables. It is possible that one variable by itself may not seem relevant, but when paired with another becomes a powerful predictor. More sophisticated approaches, which are able to better handle redundancy, include the approach of Box and Jenkins [1976] or similar time-series analysis methods, which are based on cross-correlation and partial correlation analysis. Principal component analysis (PCA) is a highly popular dimension reduction technique: it reduces \( k \) variables into \( p \) principal components based on analysis of covariance. In a number of applications, models have been developed by performing PCA and then training the ANN using the principal components as the input variables. However, the drawback of all of these approaches is that they are a legacy of linear time-series analysis, and their use is symptomatic of modellers migrating from conventional statistical modelling tools to an ANN approach by considering only ANN model architectures and learning algorithms. Use of the linear IVS techniques described above may fail to identify non-linear relationships within the data, and is essentially contradictory to the motivation for using ANN models, which is primarily to deal better with data that are presumed to describe a non-linear process.

Recently, mutual information (MI) has been found to be more suitable for the development of ANN models. Mutual information \( I \) is estimated using the expression

\[
I(X,Y) = \frac{1}{n} \sum_{i=1}^{n} \log_e \frac{p(x_i, y_i)}{p(x_i)p(y_i)}
\]

(15)
where \( p(x_i, y_i) \), \( p(x_i) \) and \( p(y_i) \) denote joint and marginal probability density functions at \( x_i \) and \( y_i \). Several IVS filters based on MI have been proposed for regression and classification applications (see Battiti [1994]; Sharma [2000]; Huang and Chow [2005]).

MI is a generic metric for dependence between variables, which is ideally suited to the development of ANNs since it can identify arbitrarily structured relationships. MI is also less sensitive to noise in the data, and is unaffected by transformations (e.g., the log transform) that might be performed during pre-processing. The drawback with MI is that, more often than not, the probability density functions are unknown and will need to be estimated from the available data. These estimates can be generated using various techniques, including histograms and kernel density estimation (KDE) [Scott, 1992]. However, density estimation is increasingly difficult for high dimensions, and significantly increases the computational effort required for an estimate of MI.

### 4.3.3 Selection with partial mutual information

An efficient forward selection filter is based on the direct estimation of partial mutual information (PMI) (also called conditional mutual information) [Sharma, 2000]. PMI is denoted as \( I(X; Y | Z) \), where \( I(X; Y) \) is conditional on variable, \( Z \). The forward selection approach iteratively selects the variable that maximises \( I(X; Y | Z) \), which is then added to the set of selected variables \( Z \). By selecting variables that maximise \( I(X; Y | Z) \), the relevance of variables is maximised using a non-linear dependence measure, but the selection of redundant input variables is avoided.

Using the approach suggested by Sharma [2000], \( I(X; Y | Z) \) is estimated from \( I(u, v) \) where \( u \) and \( v \) denote residuals determined using a regression of \( X \) and \( Y \) on \( Z \). This is analogous to estimating partial correlation, but in this case the regression is performed by non-parametric kernel regression, which can filter non-linear dependence. Kernel regression estimates for \( Y \) are given by

\[
\hat{y}(z) = \frac{1}{n} \sum_{j=1}^{n} y_j K_h(z - z_j)
\]

where \( K_h \) is the kernel function, and the residuals \( v \) are determined as \( \hat{y} - y \), and similarly for candidate \( x \). This estimation of PMI is embedded within the forward selection algorithm as follows:

1. Initialise candidate and selected input variable sets.
2. Estimate output residuals based on selected input variables.
3. For each candidate input:
   a) Estimate candidate residuals based on selected input variables.
   b) Estimate the PMI between the output and candidate residuals.
4. Find the candidate that maximises PMI.
5. Determine significance of the candidate-output PMI.
6. If the candidate is significant then:
   a) Move candidate to input variable set.
   b) Return to Step 2.
7. Else terminate selection.

The advantage over similar MI-based forward IVS algorithms, is that this approach includes a criterion to terminate the selection process, where other algorithms consider greedy selection based on a predetermined number of inputs. The termination criterion is based on the comparison of the highest PMI estimated to the upper confidence bound for the sample error in MI estimation, which is known as the critical value, or \( I^* \). Selection terminates when the estimated PMI is less than \( I^* \), indicating that
there are no more relevant variables in the remaining candidate set. However, $J^*$ cannot be directly estimated from Equation 15, and an empirical approach must be used to determine the critical value, based on bootstrap estimates of PMI for randomly ordered (i.e. independent) series, $X$ [Sharma, 2000]. The bootstrap approach can be unreliable if the bootstrap size is small, since estimates of critical value of $J$ will be inaccurate and could potentially result in an incorrect number of selections. However, large bootstrap sizes significantly increase the computational burden due to the number of MI estimates required at each iteration of the selection algorithm — especially when density estimation is required.

Several alternative termination criteria can be considered to improve accuracy and computational performance [May et al., 2008a]. If data are approximately Gaussian, then empirically derived tables of $J^*$, based on much larger bootstrap sizes, can be used in place of the bootstrap [May et al., 2006]. A second approach is to simply find the optimal trade-off in information gain versus the number of input variables selected. This can be done by measuring the Akaike Information Criterion (AIC) for the residual of the output variable, $r_i$, and terminating at the iteration corresponding to the minimum value. Finally, a third alternative termination criterion is based on the Hampel outlier test. Here, the Hampel test is used to identify whether the maximum PMI for a candidate is significantly more informative than the other candidates, which will be irrelevant.

### 4.4 Data subset selection

Data subsets selection (DSS) forms the fourth step in the overall ANN development in Figure 4.3, where the available database is split into subsets for training, testing and validation. This is to ensure the ANN model has good generalisation ability. Generalisation is a central aspect of ANN model development. Invariably, all statistical models are developed based on a finite sample of data. It is rare that data collected through observation of a process will be noise-free, and the data available for model development are likely to contain a small proportion of features that are not representative of the underlying system. Generalisation refers to the ability of a statistical model to accurately represent the underlying data-generating process, rather than the idiosyncratic features of the training data.

Figure 4.6 illustrates the concept of generalisation by considering a simple univariate regression problem. In this case the data-generating function is $F(x) = \hat{\nu}x + \epsilon$ where $\epsilon \sim N(0,0.01)$ and 50 samples are generated uniformly on the domain $[0,3]$. As shown in Figure 4.6(a), a model architecture with many parameters potentially can fit not just the underlying $\nu$ process, but also the noise in the sample of training data. Consequently, the error of estimates from the true process — the validation error — is expected to be high, and the model is said to have poor generalisation performance. A model with fewer parameters is shown in Figure 4.6(b). The degree of over-fitting in this case is reduced, although there remains some influence of the model and it is slightly over-fitted. A generalised fit is shown in Figure 4.6(c), in which the fitted model has sufficient complexity to represent the data generating process without over-fitting. Figure 4.6(d) illustrates an under-fitted model, which has insufficient complexity to wholly describe the relationship within the data.

An over-fitted model has a low error, or bias, but the error achieved will be highly dependent on the data, that is, the model error has high variance. The opposite is true for the generalised model, which has a higher bias, but which will be less sensitive to the data and will therefore have reduced variance. Ideally, the best model would have both a low error and low variance, but usually for statistical models based on a finite sample of noisy data, this is not possible. Instead, model development is required to trade-off the relative amount of bias and variance, and this is referred to as the bias-variance dilemma [Geman et al., 1992]. Generalisation for ANN models built on noisy data typically represents a trade-off in which the finite-sample variance is lowered by allowing for a bias that reflects the error due to the naturally occurring noise in the data.

Despite their many advantages over conventional statistical models, ANN models are particularly susceptible to over-fitting because of their inherent flexibility. Given a sufficient number of connection weights and sufficient training time, an ANN can represent exactly the data within the training set. Since this is not desirable, training must be undertaken using techniques that can avoid over-fitting, and ensure that the ANN generalises the underlying data-generating process.

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4.4.1 Cross-validation

Hold-out cross-validation is by far the most common approach to ANN training, as it offers the simplest approach for ensuring that generalisation is achieved when developing ANN models. In machine learning, the hold-out is synonymous with stop-training or early-stopping. In this approach, the training data are used to guide the learning process and the test error is periodically determined to ensure that the model remains general. As shown in Figure 4.7, at A the initial error for both training and test data will be poor for a randomly initialised ANN. During training, the error reduces as the ANN learns the relationships within the data until, at some point (B), the optimal generalisation performance is achieved. Further training will reduce the training error of the network, but the test error will not improve and may in fact increase as the ANN begins to overfit the training data. Given sufficient time, the ANN will be trained to perfectly represent the cases within the training data (C), but will poorly represent the underlying process. The training is therefore stopped at B to achieve the best generalisation.

ANN development requires that two hold-out datasets are generated for testing and validation. The test data are used to implement hold-out validation to avoid overfitting. However, because the minimisation of the test error is used to determine the optimal training and model parameters, the trained model is said to be optimistically biased towards the test data: that is, the error for the test data may in fact be better than the true validation error. Consequently, it is necessary to undertake an additional validation of the final ANN model, to ensure that true generalisation has been achieved, and hence validate the ANN model [Maier and Dandy, 2000].
Figure 4.7 Stop training (early-stopping) using test data to ensure generalisation during ANN training.

The primary focus of choosing a sampling technique for DSS is to ensure that the data in each subset are representative of the problem domain. An unrepresentative subset is said to be biased. Variability of model performance, due to the variability of the data subsets caused by random sampling techniques, is also a particular concern given that DSS is usually performed once during model development. Potentially, the entire model development could be jeopardised by poor partitioning into subsets. The variability of model performance due to the composition of training and test subsets is significant, and is greater than variability due to uncertainty surrounding the ANN connection weights.

The relative proportion of data in each subset is an important consideration. Although there is no consensus on the optimal proportion, it is acknowledged that too few data in any one subset will increase the chance of bias and variability. Under assumptions of uniform random sampling, the risk of bias is minimised for an equal split between each subset. However, the ANN can benefit from additional training data, and so generally more samples are allocated to the training subset. Commonly adopted proportions are 60%, 20% and 20% each for training, test and validation data subsets. Provided that a suitable sampling methodology is applied, these proportions can be used to maximise the information content within the training subset, without creating bias in the test or validation data. It is therefore important to consider the sampling technique used to perform data subset selection.

In many applications, expert judgement is used to choose the data for training, test and validation subsets. Methods based on judgement are likely to be highly biased, and results will vary from application to application as the degree of judgement and available expertise differ. Another common approach in time-series applications is to partition data into three contiguous time intervals, with the first interval used for training, the second interval for testing, and the final interval for validation. In this manner, the time-series structure is preserved, which is often desirable for trending predictions. However, this approach can be significantly biased if there are trends in the data. For example, partitioning a hydrological time series in this manner may result in testing and validation data spanning wet years, whereas the training data spans only dry years.
4.4.2 Random sampling

The simplest form of sampling is uniform random sampling, or simple random sampling (SRS). In this case, samples are drawn with equal probability, which is determined as

$$p(x \in S) = \frac{n}{N}$$  \hspace{1cm} (17)

where \( n \) is the size of sample, \( S \), and \( N \) is the number of data in the set of all available data, \( T \). Since each of the data has an equal chance of being sampled, simple random sampling is completely unbiased in its selection. However, the application of SRS to ANN development has been criticised owing to its tendency to be affected by the density distribution of the data, and it results in a poor sample when applied to non-uniform data. This is highly relevant, since most real-world applications deal with data from more natural distributions and can often be highly skewed. Also, the pure randomness of SRS results in a high degree of variability, which lowers confidence in the evaluation of ANN models based on the subsets generated.

4.4.3 Stratified sampling

Stratified sampling is a two-stage sampling technique in which the data are divided into \( H \) homogeneous groups, and then samples are drawn randomly from within each of the groups. Provided that strata are sufficiently homogeneous, the benefit of stratified sampling is that a representative sample can be drawn, since data are guaranteed to be drawn throughout the entire problem domain. The most important issue is how to stratify the data, especially in the case of multivariate datasets.

The self-organising map (SOM) [Kohonen, 1995] has been found to be a particularly good tool for performing stratified sampling in ANN development [Bowden et al., 2002; Anctil and Lauzon, 2004]. This technique is referred to as SOM-based stratified sampling (SBSS), and is illustrated in Figure 4.8. The SOM projects the data onto an \( r \times c \) grid, where each cell corresponds to one of \( H \) strata, and data in each map unit are then allocated into training, test and validation subsets. The robustness of the SOM as a tool for partitioning data, combined with the benefits of stratified sampling, makes this a particularly effective approach to DSS. However, it is necessary to specify the size of the SOM and choose an appropriate sampling technique for selecting data from within each partition.

![Figure 4.8 Stratified sampling based on the self-organising map](image)

The Neyman allocation rule can be used to determine the number of samples. According to this rule, the number of data drawn from within each SOM partition, \( n_h \), is determined as...
where \( \sigma_j \) is the intra-stratum standard deviation. The Neyman allocation rule results in a more representative sample because it accounts for differences in both the number of data within each SOM partition, and the relative spread of data. This is important, since the partitions generated by the SOM roughly approximate the density distribution of the data, and so some partitions will contain many, densely distributed data; whereas other partitions may contain fewer, more sparsely distributed data.

In traditional cluster analysis, the number of SOM units can be determined by measuring the separation and compactness of the clusters formed by the partitioning. Cluster validity measures, such as the silhouette coefficient \( S \) [Kaufman and Rousseeuw, 1990], have been considered as a means of determining the optimal number of SOM partitions in several applications [Shahin et al., 2004; Kingston, 2006]. However, in DSS the data may not necessarily be strongly clustered, or have only one or two large natural clusters. If the data are not strongly clustered, then analysis of cluster validity may be inherently difficult. In the case of a few large clusters, the predicted SOM size will accordingly be very small, and this will lead to few partitions, each with a large number of data, and would not yield a significant improvement over simple random sampling. However, it can be shown for DSS that a SOM with the number of units

\[
k \approx N^{0.54},
\]

which is a rule-of-thumb recommended by Vesanto [1999], yields effective sampling when using Neyman allocation. At least this number of SOM units is required to achieve good sampling, by providing a sufficient number of homogeneous groups from which to draw a sample. Given the SOM width-to-length ratio \( \gamma \), and \( k = mn \), the number of map units can be therefore be written, in terms of \( m \), as

\[
k = \frac{m^2}{\gamma}
\]

which can then be substituted into Equation 19 to give the required number of SOM rows as

\[
m = \sqrt{\gamma \beta}N^{0.54}
\]

### 4.4.4 Systematic sampling

Systematic sampling is a non-probability sampling method, in which every \( k^{th} \) sample is selected. Given \( n \) samples to be drawn, the sampling interval \( k = \frac{N}{n} \) is determined. The first sampling location is chosen by drawing a random location \( m \in [1, k] \) and then sampling locations \( m + k, m + 2k, \ldots \) etc. If the data are unordered, then systematic sampling yields a uniformly random sample. However, care must be taken to avoid unknowingly biasing a systematic sample, which can occur if the data are somehow structured and the sampling interval aligns with this structure. For example, sampling a daily time series at a weekly interval might only capture weekend information.

Sorting the data according to one variable (usually the output variable), prior to systematic sampling, implicitly stratifies the data along that variable, and this is called systematic stratified sampling. Baxter et al. [1999] used such an approach to generate ANN training data for a water quality model. However, the methodology is not well suited to multivariate datasets, since it cannot guarantee representative sampling of regions of the input domain that might lead to an equivalent output variable.

### 4.4.5 DUPLEX

DUPLEX [Snee, 1977] is a deterministic algorithm for choosing calibration and test subsets, and is particularly popular in chemometrics [Despagn and Massart, 1998]. The DUPLEX algorithm is based on Kennard-Stone sampling and proceeds as follows:
1. Find $x_i$ and $x_j$ that maximise $|x_i - x_j|$ and move from $T$ to training set.

2. Find $x_k$ and $x_l$ that maximise $|x_k - x_l|$ and move from $T$ to test set.

3. Find next sampled pair $x_m$ and $x_n$, such that they maximise the minimum single-linkage distance $|x - s|$ for $s \in S$.

4. Repeat, alternating allocation between training and test samples, until smallest set is filled.

5. Allocate all remaining samples to the larger set.

Provided that the database is convex and relatively uniformly distributed, the DUPLEX algorithm provides an effective way to ensure that representative data subsets are selected. Unlike probabilistic techniques, DUPLEX is deterministic and therefore overcomes the issue of sample variability. However, the computational requirement of the algorithm will increase as the database length becomes large, which limits the application of the approach to moderately sized datasets.

4.4.6 Search optimisation

The potential application of optimisation algorithms to DSS has been considered in two examples where, in each case, a genetic algorithm (GA) was used to improve on trial-and-error sampling and evaluation of data subsets. One approach is to use a GA to optimise subsets based on model performance [Reeves and Taylor, 1998], in which essentially the IVS wrapper approach applied to DSS. This approach, while able to find subsets that lead to good model error, leads to the computational burden of wrapper strategies. On the other hand, a GA can be formulated where the objective function is based on statistical evaluation of the subsets [Bowden et al., 2002, 2006].

4.4.7 Choosing a sampling technique

Despite being widely used, simple random sampling (SRS) is unreliable and is not recommended as a technique for DSS when applied to real-world datasets. As an alternative, either stratified sampling, based on the SOM, or, DUPLEX sampling, can be recommended for generating representative subsets for ANN development. The stratified sampling approach scales well, and would be used preferentially for large databases, or for databases with non-uniformly distributed data. Otherwise, the DUPLEX algorithm has the advantage of drawing representative data with zero variability, which can increase confidence in subsequent performance assessment based on training, test and validation data subsets.

In the case of bivariate datasets, the systematic stratified approach can also be effective, and can be more easily implemented than the SOM-based or DUPLEX algorithms. However, because the implicit stratification on the output variable is unable to take into account all input-output tuplets, the technique cannot be guaranteed to provide the same results for higher-dimensional datasets.

The application of optimisation algorithms to DSS is dependent on an appropriate and efficient method for the evaluation of the data subsets. The link between similarity of global statistics and the representativeness of data is somewhat tenuous and has yet to be proven. Consequently, additional investigations of suitable methods for data subset evaluation are warranted to develop this approach further before it would be recommended for DSS.

4.5 Training

The ability of ANN architectures to learn patterns within data from a set of training examples underpins the machine-learning paradigm. In model development the focus is on supervised learning, where the initially random weights of the ANN are iteratively adjusted according to the network prediction error. In this sense, ANN training is analogous to the calibration or estimation of parameters that is undertaken during the development of more conventional models.

4.5.1 Backpropagation algorithm

The back-propagation algorithm (BPA) [Rumelhart et al., 1986] is credited as the first training algorithm developed, and was the first example of how ANN architectures could be used to learn. The
The basic principle behind the algorithm is that the global error of each network layer is the result of erroneous signals from preceding layers. During training, patterns are iteratively presented to the network, and the network response is compared to the target response corresponding to the input vector. In order to correct the network, the error determined during training is fed backwards to each of the nodes, and the connection weight for each node is adjusted based on both the direction and magnitude of the error, and the magnitude of the weight applied. This is expressed according to the weight update rule

$$w_{ij}(t + 1) = w_{ij}(t) - \eta \frac{\partial E}{\partial w_{ij}(t)}$$

(22)

where $\eta$ is the learning rate and $t$ denotes the training iteration. The standard BPA described updates the weights after each training example is presented, and this is referred to as online training. However, it is often considered beneficial to back-propagate an aggregate error that is based on several examples, and this is referred to as batch training, where the number of samples presented before updating is the epoch size. Depending on the degree of noise in the data, batch training can reduce the number of iterations required to reach convergence by smoothing the effects of spurious data.

Despite the machine-learning paradigms that are often used to describe MLP training, the BPA and similarly derived MLP training algorithms, are essentially a form of gradient descent optimisation, in which the weights are adjusted according to the slope (i.e. gradient) of the training error with respect to the weights. A common pitfall of gradient descent optimisation algorithms is that they are prone to suboptimal convergence when applied to functions that have complex error surfaces with many local optima. As illustrated in Figure 4.9, depending on the initialisation of the network, an MLP trained by the back-propagation algorithm could converge at any number of locally optimal conditions, rather than the globally optimum set of weights. Consequently, a common variation to the standard BPA is the use of a momentum heuristic, for which the modified weight update rule is given by

$$\Delta w_{ij}(t + 1) = w_{ij}(t) - \eta \frac{\partial E}{\partial w_{ij}(t)} + \lambda \Delta w_{ij}(t)$$

(23)

Here, the momentum term $\lambda$ is intended to address the issue of sub-optimal convergence to local minima by additionally adjusting weights by an amount that aggregates successive iterations. The effect is to ensure that the training is less sensitive to small local changes in the error surface. This is also illustrated in Figure 4.9.

Successful training of an MLP using BPA is dependent on using appropriate values for $\eta$ and $\lambda$. A learning rate that is large will generate erratic changes in weights, and the network will be slow to converge; however, a learning that is too small will also result in slow convergence due to slow training. A large momentum will help ensure that suboptimal convergence is avoided, but a momentum that is too high will adversely affect convergence to the optimum solution. Maier and Dandy [1997] suggest that a small learning rate of around 0.05–0.1 in conjunction with a momentum of 0.8–0.9 will achieve reasonable results. However, it is also recommended that some fine tuning of these parameters is necessary, which can be beneficial in ensuring that the best results are obtained for the training dataset at hand.
4.5.2 Evolutionary algorithms

Heuristics, such as momentum, can assist in avoiding the pitfalls of gradient descent optimisation, but still provide no guarantee that the network will converge at or near the global optimum. Consequently, the application of evolutionary and stochastic optimisation algorithms to ANN training has generated a great deal of interest.

The formulation of ANN training as an optimisation problem is the same as that applied to calibration of other types of models. In the case of ANNs, the network weights are optimised to minimise the training error. Optimisation strategies that have been successfully applied to MLP training include genetic algorithms (GAs) ant colony optimisation (ACO), shuffled complex evolution (SCE) and simulating annealing. These optimisation algorithms are particularly adept at finding near-global optimal solutions for problems that have a large number of decision variables and a complex error surface. This makes them an ideal algorithm for ANN training, especially for larger network architectures, since they can efficiently search through the large combination of possible weight values, and are generally insensitive to local optima.

Taking the evolutionary approach further, the algorithm may be implemented to also take into account the choice of input variables and network size, in which case all aspects of the network architecture are determined through the optimisation. These are often referred to as evolutionary artificial neural networks (EANNs).

4.5.3 Brent’s algorithm

In contrast to the MLP, the GRNN is considered to be a lazy-learner: that is, the network queries the training data each time an input pattern is presented to the network, in order to determine the network output. Training of a GRNN is very fast in comparison to an MLP, since only the kernel bandwidth needs to be optimised. The error curve for the GRNN has a single optimum value, about which the error curve is relatively smooth and continuous. Any number of one-dimensional optimisation approaches can be used, including hill climbing, gradient descent, and interval halving. It should also be noted that GRNN training is equivalent to the cross-validation (CV) bandwidth selection problem for kernel regression.

Bowden et al. [2006] proposed Brent’s algorithm [Brent, 1973] as a fast training algorithm for the GRNN network. Brent’s algorithm is a fast, one-dimensional optimisation algorithm, which relies on successive quadratic interpolation to determine the optimum value of a function. Brent’s algorithm therefore assumes that the function is sufficiently smooth and parabolic within the neighbourhood of the optimum, which is a reasonable assumption in the case of the GRNN error function [Caudill, 1993].
Given a triplet of points \( x_a < x_c < x_b \) such that \( f(x_a) \geq f(x_c) \) and \( f(x_b) \geq f(x_c) \), quadratic interpolation estimates the minimum of \( f \) on \([a, b]\) as the minimum of a parabola fitted through the function at \( x_a, x_b \) and \( x_c \) [Press et al., 1992]. The value of \( x_q \), at which the minimum of the parabola occurs, can be determined directly from the quadratic formula as

\[
x_q = \frac{x_a f(x_b)f(x_c) + x_b f(x_a)f(x_c) + x_c f(x_a)f(x_b)}{[f(x_a) - f(x_b)][f(x_a) - f(x_c)]}
\]

However, quadratic interpolation is only possible provided that \( c \neq a \) and \( c \neq b \). If this is not the case, Brent’s method alternatively tries to find the next trial solution using the secant rule, which is given as

\[
x_s = b - \frac{f(b) - f(a)}{f(b) - f(a)}
\]

Solutions for either quadratic interpolation or the secant rule must satisfy the feasibility constraints:

\[
\frac{3x_b + x_c}{4} < x_s \leq x_c
\]

\[
|x_s - x_b| \geq \frac{|x_b - x_c|}{2}, \text{ and}
\]

\[
|x_s - x_b| \geq \frac{|x_b - x_d|}{2},
\]

Otherwise, Brent’s algorithm defaults to interval halving, and the next guess becomes the midpoint, \( x_m \), of the interval \([a, b]\).

The key to implementing Brent’s algorithm is in determining the initial bracketing triplet \( x_a, x_b \) and \( x_c \), which is difficult if \( f \) is unknown, and one strategy is to adopt a trial-and-error approach using Golden search [Bowden, 2003; Press et al., 1992] until a suitable triplet is found. However, this method can be improved by making use of the Gaussian kernel reference bandwidth, which is given as [Silverman, 1986]

\[
h^* = \left(\frac{1}{4\pi}\right)^{1/(d+4)} \sigma n^{-1/(d+4)},
\]

where \( \sigma \) is the sample standard deviation of the data, \( n \) is the number of training patterns and \( d \) is the input dimensionality. The reference bandwidth is the theoretical optimal bandwidth, assuming that the data are Gaussian. However, in most cases although \( h^* \) is near the optimum bandwidth, it is typically found to over-smooth (i.e. it is too large), which suggests that a bracketing of the optimal bandwidth should fall on the interval \([0, kh^*]\) where \( k \geq 1 \). A conservative bracketing can be obtained by using \( h^* \) as the initial guess, and taking points either side. In this case, the Golden ratio \( \psi \) can be applied, so that the initial bracketing is \( 0, kh^*, \psi h^* \).
4.6 Model selection

In the case of some ANN architectures, it is often necessary to specify the internal architecture of the network. The most common example is the multilayer perceptron (MLP), which can have any number of layers, each with any number of neurons. Considering that the network is restricted to three layers, and the network is fully connected, then only the number of hidden nodes, \( N_H \), needs to be specified. There are no rules that can be used to determine the optimal number of hidden nodes, as this will depend on issues specific to the application and to the data, and so a trial-and-error approach is required to evaluate multiple networks constructed for a range of hidden layer sizes. Some guidelines have been developed that can be used to place an upper bound on the number of hidden nodes, \( N_H \), such that the range of sizes to be evaluated is restricted to \([1, N_H]\).

Simply choosing the model that results in the minimum error, while straightforward to implement, is often a poor method for selecting the best ANN model. Because of a larger number of parameters, models with a greater number of hidden nodes can often yield a low error, but are somewhat optimistic in a statistical sense. Instead, model selection criteria should be used that can determine the optimal trade-off between model accuracy and parsimony. Criteria such as the Akaike Information Criterion (AIC) and Schwarz’s Bayesian Information Criterion (BIC) should be considered to compare the performance of models of different sizes, since these each penalise models of increasing complexity. These are determined, respectively, by the following expressions:

\[
AIC = n \log \left( \frac{1}{n} \sum_{i=1}^{n} (y_i - \hat{y}_i)^2 \right) + 2p, \quad \text{and} \\
BIC = n \log \left( \frac{1}{n} \sum_{i=1}^{n} (y_i - \hat{y}_i)^2 \right) + n \log n,
\]

where \( p \) is the number of model parameters.

4.7 Validation

The final step in model development is to validate the model. Model validation is necessary for providing an expectation of model performance post-deployment, when the model will face previously unseen data. The assessment of performance is based on the model performance when querying the validation data, which is used in neither training nor model selection stages, yet provide a representative sample of the modelling problem domain.

4.7.1 Performance criteria

Several performance criteria are commonly used to assess the accuracy of an ANN, based on comparison of the ANN estimates with known or target values. The mean squared error (MSE) or the root mean squared error (RMS) are often used as the error function during training. These are given, respectively, as follows:

\[
MSE = \frac{1}{n} \sum_{i=1}^{n} (y_i - \hat{y}_i)^2
\]

\[
RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (y_i - \hat{y}_i)^2}
\]
DEVELOPMENT OF TOOLS FOR IMPROVED DISINFECTION CONTROL WITHIN DISTRIBUTION SYSTEMS

In both expressions, the squared error term heavily penalises predictions that are highly erroneous. Other measures such as the mean absolute error (MAE) and mean relative error (MRE) are used to further evaluate a trained model, and are given by the expressions

\[
MAE = \frac{1}{n} \sum_{i=1}^{n} |y_i - \hat{y}_i|, \quad \text{and}
\]

\[
MRE = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{y_i - \hat{y}_i}{y_i} \right|
\]

These measures provide an indication of the magnitude of predictions in absolute or relative terms, respectively. The MRE can also indicate any bias, either as an underprediction, or an overprediction, which may impact on the evaluation of the ANN. Finally, in statistical modelling it is common to use goodness-of-fit measures to describe how well model estimates describe the targets. The coefficient of determination \( r^2 \) is the most common example, and is given as

\[
r^2 = \frac{\sum_{i=1}^{n} (y_i - \bar{y})(\hat{y}_i - \bar{y})}{\sqrt{\sum_{i=1}^{n} (y_i - \bar{y})^2 \sum_{i=1}^{n} (\hat{y}_i - \bar{y})^2}}
\]

4.7.2 Fitness for purpose

In general terms, the goal is to strive for the most accurate model that can be achieved with the available data. However, another good test of a model is whether or not it is suitable for its intended purpose. This can be determined by real-world or simulated deployment of the model within an application, and observation of the application performance. For example, if the model is intended for use within a control loop, then the performance measure is the set-point tracking provided by the controller. This is important, since some applications may be robust, while others may be intolerant of errors in the model predictions. The modeller should be well aware of these considerations, as it is often useful to avoid investing too much time honing the ANN development to reduce the statistical error, if it does not improve the utility of the end-use application.

4.7.3 Naïve model benchmark

A common benchmark comparison in time-series analysis is to consider the relative improvement in prediction accuracy with a naïve model. For a single-step forecast, a naïve model is simply \( \hat{y}(t) = y(t - 1) \); that is, the estimate of next state will be the last known state. The reason for this comparison is that the accuracy of predictive models based on a long time-series can be deceptive, since correlation between a one-step phase (i.e. a naive prediction) will most likely be high. The investment of resources required to develop an ANN time-series model can only be justified if the predictions improve on a naïve model.

4.7.4 Sensitivity/importance analysis

Sensitivity and importance analysis of a trained ANN provide diagnostic tools that can be used to identify the relationships determined by the ANN during training. This type of analysis is often the primary motivation in knowledge extraction applications, where these relationships are unknown prior to model development. Where there is already some basic understanding of the relationships within a modelled system, these tools can be used to verify that the relationships captured within the ANN weights correspond to the known behaviour of the system. Given the flexibility of ANN models, there is often a concern that they may behave unpredictably, and so verifying of the plausibility of the model is a useful addition to the validation step [Kingston et al., 2006a].
Sensitivity analysis is usually performed by varying an input over its natural range, while holding other input variables steady. Because the sensitivity of the output can depend on the model state, the sensitivity analysis is repeated over a range of fixed input values, and for each input variable. Both the relative magnitude and direction in the ANN response can be compared with the variation in the input to determine the influence of the input variables. However, the limitation is that by varying only one variable at a time, the analysis potentially overlooks synergism between input variables, and may therefore underestimate their importance.

Importance analysis determines the overall influence of input variables by considering the input-output connections that are encapsulated in the weights of the trained ANN. In the modified connection weight approach [Kingston et al., 2006a], the relative importance (RI) is determined as

\[
RI_i = \frac{OCW_i}{\sum_{j=1}^{N_H}|OCW_j|} \times 100%\]

where \(OCW_i\) is the connection strength given by

\[
OCW_i = \sum_{j=1}^{N_H} f(w_{ij})v_j
\]

Here, \(f\) is the transfer function and \(w_{ij}\) and \(v_j\) denote the connection weights between the layers of the ANN. The connection strength is determined, with respect to each input variable, and then normalised in Equation 37 to calculate the RI.

As an alternative approach, the relative strength of the input variables can also be inferred by the relative PMI for each input variable determined during the IVS step. Soofi et al. [2000] show that the importance of each variable can be estimated according to

\[
RI = \frac{I'(X_i, Y|X)}{\sum_{j=1}^{N} I'(X_j, Y|X)} \times 100%\]

where \(I'(X_i, Y|X)\) is the PMI between candidate \(X_i\) and \(Y\) conditional of selected input variable set \(X\), which is estimated at each iteration of the partial mutual information selection (PMIS) algorithm. Kingston et al. [2006a] found that this measure compared well with methods based on analysis of the ANN weights. This result is useful, since this knowledge can be obtained prior to the training of an ANN, and is independent of the architecture. The RI gained from the PMI of input variables can be useful information in itself, or in further ensuring that the ANN has learnt the true relationships, by comparing this initial assessment of input importance with the assessment of the ANN after training.

**5 DISINFECTANT RESIDUAL FORECASTING**

The following case study describes the application of the ANN development methodology, where a GRNN is applied to forecasting water quality within a real-world water distribution system. In this case, the study demonstrates the benefits of the input variable selection (IVS) approach for this application.

**5.1 System description**

The Myponga water treatment plant is managed and operated by United Water International Pty Ltd under contract with the state regulatory authority, SA Water. The plant is situated 60 km to the south of Adelaide, South Australia, adjacent to the Myponga Reservoir, from which the plant is supplied with raw water. The treatment process combines alum flocculation with dissolved air flotation and rapid dual-media filtration. Post-filtration, the pH is corrected by caustic dosing, and the filtered water is then disinfected by a chlorine injection system that is flow-paced to achieve a set-point free chlorine concentration, which is specified by the plant operator. Following a short detention time in a contact tank, the finished water flows into the filtered water storage tanks, from which the water flows under
gravity via a trunk main, which supplies several branched reticulation systems. The plant does not have provision for booster chlorination at the outlet of the filtered water storage tanks. However, the primary chlorinator set-point, which is determined by the WTP operators, is considered to provide a sufficient dose to maintain minimum free chlorine residuals at the extremities of the distribution system. Due to this configuration, fluctuations in detention time within the filtered water storage tanks can have a significant impact on the free chlorine residuals that are observed downstream.

In this case study, ANN models were developed to forecast residual concentrations of free chlorine 24-hours in advance, at a monitoring location that was situated at a branch location on the trunk main, approximately 20 km downstream of the filtered water storage tanks.

5.2 Data collection and pre-processing

A six-month period of monitoring and data collection was undertaken between December 2002 (Summer) and July 2003 (Winter) to obtain a database for model development. Several sources of on-line operational data were available from routine monitoring, including: turbidity of the filtered water, corrected pH, free chlorine residual immediately downstream of the primary injection point (surrogate for applied primary dose), free chlorine downstream of the filtered water storage tanks, filtered water storage outlet flow rate, and filtered water storage level. An additional sensor was temporarily installed at the downstream forecasting location on the trunk main, which provided on-line measurement of both free chlorine and water temperature. A statistical summary of the data collected for each of the monitored hydraulic and water quality parameters is provided in Table 4.1. Although the data do not span the full year as recommended by Serodes et al. [2001], the period was considered sufficient to build a training database that captured both summer and winter seasonal operational conditions, that is, the range of the data collected encompassed all possible extreme operating conditions.

The raw data interval varied across different parameters from 10 to 15 minutes, although in this study the data were aggregated during pre-processing to the average over an hourly interval for all variables.

The data were then examined to check for any erroneous values, or gaps, that may have been caused by instrument or telemetry failure. For singular erroneous values, and for small gaps of one to two records in length, data were infilled using the average of values either side of the break, or by extrapolating previous values. In the event of longer periods of missing data, the entire record was deemed unusable and was removed from the database. After constructing the 24-hour forecast time-series of the downstream chlorine residual, and lags of up to 48 hours for each parameter, the available modelling data comprised a total of 2773 hourly records.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variable</th>
<th>Min</th>
<th>Max</th>
<th>Ave</th>
<th>St. Dev.</th>
<th>25%-ile</th>
<th>75%-ile</th>
<th>Interquartile range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary free chlorine (mg/L)</td>
<td>C_{WTP}</td>
<td>0.000</td>
<td>6.49</td>
<td>3.17</td>
<td>0.62</td>
<td>3.04</td>
<td>3.48</td>
<td>0.44</td>
</tr>
<tr>
<td>Filtered water pH</td>
<td>pH</td>
<td>5.34</td>
<td>14.00</td>
<td>7.19</td>
<td>0.22</td>
<td>7.14</td>
<td>7.25</td>
<td>0.11</td>
</tr>
<tr>
<td>Filtered water turbidity (NTU)</td>
<td>Tu</td>
<td>0.00</td>
<td>2.00</td>
<td>0.06</td>
<td>0.07</td>
<td>0.04</td>
<td>0.08</td>
<td>-0.04</td>
</tr>
<tr>
<td>FWS tank level (%)</td>
<td>H</td>
<td>43.39</td>
<td>100.00</td>
<td>78.61</td>
<td>9.24</td>
<td>72.39</td>
<td>85.87</td>
<td>13.48</td>
</tr>
<tr>
<td>FWS outlet free chlorine (mg/L)</td>
<td>C_{FWS}</td>
<td>1.03</td>
<td>2.59</td>
<td>2.01</td>
<td>0.26</td>
<td>1.85</td>
<td>2.22</td>
<td>0.37</td>
</tr>
<tr>
<td>FWS outlet flow (ML/d)</td>
<td>Q</td>
<td>6.31</td>
<td>51.54</td>
<td>17.37</td>
<td>7.73</td>
<td>10.42</td>
<td>23.48</td>
<td>13.06</td>
</tr>
<tr>
<td>Water temperature (deg C)</td>
<td>T</td>
<td>11.03</td>
<td>26.30</td>
<td>16.75</td>
<td>3.51</td>
<td>13.13</td>
<td>19.60</td>
<td>6.47</td>
</tr>
<tr>
<td>Downstream free chlorine (mg/L)</td>
<td>C_{WDS}</td>
<td>0.12</td>
<td>1.87</td>
<td>0.75</td>
<td>0.33</td>
<td>0.50</td>
<td>0.97</td>
<td>0.47</td>
</tr>
</tbody>
</table>
6 DATA SUBSETS

The attributes of the data were a dense, smoothly distributed, with a single highly relevant input; and since no data reduction was employed, a relatively large number of data points was available. Consequently, there was considered little advantage in employing a stratified technique, and so simple random sampling was used to partition the data. In this study, the respective proportions of samples were allocated randomly to each of the training, testing and validation subsets were:

- 64% training,
- 16% testing, and
- 20% validation.

However, in order to account for any potential variance in model performance that could be attributed to the sampling procedure, ensemble training was used, in which an ensemble of GRNN models was trained based on independent resamplings of the data. Uniform random sampling of the data was used to sample 100 instances of data subsets according to the specified proportions. A GRNN was then trained on each instance of training and test data, and queried against the corresponding validation set. The aggregate (mean) validation performance for all models then provided an indication of the expected model performance, and the variance could confirm the confidence bounds to allow comparisons between different models. Ensemble training is an effective means of accounting for sample variance in the performance of models, which can potentially be introduced by the hold-out cross-validation procedure [Anctil and Lauzon, 2004]. All data are used during training, including extreme cases, so that no information is lost due to the hold-out.

6.1 Selected input variables

The modified PMIS algorithm described in Section 4.3.3 was applied to select a set of input variables from the 384 candidate variables available for inclusion. The results of the analysis are summarised in Table 4.2, which indicates the PMI corresponding to the most relevant variable identified at each iteration. The AIC-based termination criterion resulted in the selection of 10 input variables. Use of the Hampel-test based termination criterion resulted in the selection of the first four input variables, with subsequent variables failing the significance test. An immediate observation is that neither set of input variables includes flow rate, pH, or turbidity. Rather, the selected input sets describe a predominantly auto-regressive time-series structure within the data, with a small contribution from exogenous lags of upstream chlorine and water temperature.

**Table 4.2 PMIS analysis of input variables for the Myponga trunk main case study.**

<table>
<thead>
<tr>
<th>Iteration</th>
<th>Candidate</th>
<th>PMI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C_{WDS}(t)</td>
<td>1.087</td>
</tr>
<tr>
<td>2</td>
<td>C_{FWS}(t)</td>
<td>0.105</td>
</tr>
<tr>
<td>3</td>
<td>T(t – 13)</td>
<td>0.106</td>
</tr>
<tr>
<td>4</td>
<td>C_{WDS}(t – 24)</td>
<td>0.090</td>
</tr>
<tr>
<td>5</td>
<td>C_{WDS}(t – 47)</td>
<td>0.074</td>
</tr>
<tr>
<td>6</td>
<td>C_{WDS}(t – 3)</td>
<td>0.070</td>
</tr>
<tr>
<td>7</td>
<td>C_{WTP}(t)</td>
<td>0.065</td>
</tr>
<tr>
<td>8</td>
<td>C_{FWS}(t – 17)</td>
<td>0.062</td>
</tr>
<tr>
<td>9</td>
<td>C_{WDS}(t – 27)</td>
<td>0.062</td>
</tr>
<tr>
<td>10</td>
<td>C_{WDS}(t – 1)</td>
<td>0.071</td>
</tr>
</tbody>
</table>

**Table 4.3 Summary of input variables selected for GRNN models of the Myponga WDS**

<table>
<thead>
<tr>
<th>Model</th>
<th># Inputs</th>
<th>Inputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10</td>
<td>C_{WDS}(t), C_{FWS}(t), T(t – 13), C_{WDS}(t – 24), C_{FWS}(t – 47), C_{WDS}(t – 3), C_{WTP}(t), C_{FWS}(t – 17), C_{WDS}(t – 27), C_{WDS}(t – 1)</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>C_{WDS}(t), C_{FWS}(t), T(t – 13), C_{WDS}(t – 24)</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>C_{WTP}(t), pH(t), Tu(t), C_{FWS}(t), Q(t), T(t), C_{WDS}(t)</td>
</tr>
<tr>
<td>D</td>
<td>384</td>
<td>C_{WTP}, pH, Tu, C_{FWS}, Q, T, C_{WDS} v(t, . . . , t – 48)</td>
</tr>
</tbody>
</table>
Models developed using the input sets selected using PMIS with the AIC-based and Hampel test-based termination criteria are denoted as Models A and B, respectively. Additional input variable sets—one consisting of all available parameters at time $t$ only, and the other comprising all available lags ($t, \ldots, t - 48$)—were considered for comparison purposes. The models corresponding to these input variable sets are denoted as Models C and D, respectively. The input sets corresponding to all models are summarised in Table 4.3.

### 6.2 Data sampling

In this case study, the respective proportions of samples allocated to each of the training, testing and validation subsets were:

- 64% training,
- 16% testing, and
- 20% validation.

The model was split using random sampling. Due to the data having one highly influential input, uniform distribution of the data, and a large number of data points, there was little gain in applying a stratified data sampling technique. In order to account for any potential variance or bias in model performance that could be attributed to the sampling procedure, ensemble training was used, in which an ensemble of GRNN models was trained based on independent resamplings of the data. Uniform random sampling of the data was used to sample 100 instances of data subsets according to the specified proportions.

**Table 4.4** Test performance for 24-hour forecasts of residual chlorine within the Myponga WDS.

<table>
<thead>
<tr>
<th>Model</th>
<th>RMSE* (mg/L)</th>
<th>MAE* (mg/L)</th>
<th>MRE*</th>
<th>$r^2$*</th>
<th>AIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model A</td>
<td>0.0550 (0.0108)</td>
<td>0.0330 (0.0077)</td>
<td>0.0531 (0.0123)</td>
<td>0.9862 (0.0056)</td>
<td>13.5</td>
</tr>
<tr>
<td>Model B</td>
<td>0.0657 (0.0060)</td>
<td>0.0385 (0.0033)</td>
<td>0.0628 (0.0058)</td>
<td>0.9808 (0.0039)</td>
<td>7.6</td>
</tr>
<tr>
<td>Model C</td>
<td>0.1027 (0.0149)</td>
<td>0.0610 (0.0101)</td>
<td>0.1000 (0.0181)</td>
<td>0.9525 (0.0136)</td>
<td>14.0</td>
</tr>
<tr>
<td>Model D</td>
<td>0.1022 (0.0562)</td>
<td>0.0724 (0.0149)</td>
<td>0.0823 (0.0381)</td>
<td>0.8952 (0.0251)</td>
<td>768.0</td>
</tr>
</tbody>
</table>

*Values in parentheses denote standard deviation.

A GRNN was then trained on each instance of training and test data, and queried against the corresponding validation set. The aggregate (mean) validation performance for all models then provided an indication of the expected model performance, and the variance could confirm the confidence bounds to allow comparisons between different models. Ensemble training is an effective means of handling any sample bias and variance in the performance of models, which can potentially be introduced by the holdout cross-validation procedure [Anctil and Lauzon, 2004]. All data are used during training, including extreme cases, so that no information is lost due to the hold-out.

### 6.3 Model performance

The performance of GRNN models developed using the inputs in Table 4.3 are summarised in Table 4.4 and Table 4.5 for test and validation data, respectively. Each table shows the average error for the ensemble of GRNN models trained on independent data subsets. The standard deviation of results in both test and validation results was low, which indicates the results for each individual GRNN in the ensemble trained on independent samples has low sample variability. This was confirmed by a $t$-test, comparing the performance on the model performances, which indicated that the variance was insignificant.

In terms of accuracy alone, the best performance was obtained by Model A, which used ten input variables selected by PMIS with the AIC-based termination criterion. This model had the lowest average RMSE (0.055 mg/L). However, comparison of the corresponding AIC values indicates that the
smaller set of inputs used in Model B resulted in a more efficient model. The results for Model C indicate that the GRNN with no lagged input variables performed poorly, with an error approximately twice that of models A and B. Model D had the worst validation performance, with the highest MAE (0.0746 mg/L) and the lowest $r^2$ value of 0.8879, which shows that, for real-world data that contain noise, models using a large input variable set can perform worse than those with fewer inputs, and that inclusion of superfluous variables can reduce model performance.

The ability of Model B to forecast chlorine disinfectant residuals 24 hours in advance is illustrated in Figure 4.10 on page 34, which shows a portion of the original time-series, $C_{WDS}(t)$, as a solid line, with corresponding test and validation forecasts generated by Model B (for one instance of training, test and validation data). It should be noted that it is necessary to plot the forecasts in this way, as the time-series order of data was not preserved in test and validation data subsets due to the random sampling procedure used for hold-out validation.

Table 4.5 Validation performance for 24-hour forecasts of residual chlorine within the Myponga WDS.

<table>
<thead>
<tr>
<th>Model</th>
<th>RMSE* (mg/L)</th>
<th>MAE* (mg/L)</th>
<th>MRE*</th>
<th>$r^2*$</th>
<th>AIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model A</td>
<td>0.0654 (0.0142)</td>
<td>0.0342 (0.0062)</td>
<td>0.0550 (0.0103)</td>
<td>0.9805 (0.0095)</td>
<td>13.6</td>
</tr>
<tr>
<td>Model B</td>
<td>0.0695 (0.0075)</td>
<td>0.0388 (0.0024)</td>
<td>0.0634 (0.0044)</td>
<td>0.9784 (0.0046)</td>
<td>7.7</td>
</tr>
<tr>
<td>Model C</td>
<td>0.1159 (0.0185)</td>
<td>0.0633 (0.009)</td>
<td>0.1024 (0.0188)</td>
<td>0.9390 (0.02)</td>
<td>14.1</td>
</tr>
<tr>
<td>Model D</td>
<td>0.1061 (0.0595)</td>
<td>0.0746 (0.0133)</td>
<td>0.0844 (0.0391)</td>
<td>0.8879 (0.025)</td>
<td>768.1</td>
</tr>
</tbody>
</table>

*Values in parentheses denote standard deviation.

Figure 4.10 24-hour test and validation forecasts of free chlorine residual generated by Model B for an instance of training, test and validation data.

Overall, the results obtained are comparable to those reported previously by Serodes et al. [2001] and Bowden et al. [2006] for similar applications, and support the suitability of sparse ANN models, which utilise a minimum set of input variables, for generating forecasts of residual chlorine within distribution systems. Potential applications include the development of early warning systems that are able to predict fluctuations in downstream water quality in advance, in order to allow operators to make any necessary adjustments to the chlorine dose.
6.4 Discussion

6.4.1 Model parsimony

The results of the case studies presented in this paper support the finding by Serodes et al. [2001] that maximising the available information regarding the dynamics of the WDS leads to optimal model performance. The process delays and detention times within a WDS can be long (up to several days), and the ANN needs to contain sufficient input variables to capture the dynamics over this period to generate the best possible forecasts. However, the case study presented in this paper has also demonstrated that, while the inclusion of dynamic variables is important, there are many redundant and irrelevant parameters that can be excluded from the ANN model without sacrificing forecasting accuracy. Given the importance of selecting as few inputs as possible, there is a clear case for utilising an algorithm such as PMIS during ANN development.

Based on the results, neither of the two PMIS termination criteria used were found to clearly perform better than the other, and the use of each criterion resulted in an accurate model that incorporated a relatively efficient subset of the entire lagging window. Models that were developed with inputs selected using PMIS compared favourably with models that utilised no lagged variables, and those using all lagged variables, although there were differences in each case study between the number of input variables selected. Given the potential size of the lagging window and the large number of candidate input variables, the difference in efficiency will be relatively small in comparison to the overall efficiency gained by the use of PMIS. This study has demonstrated that the criteria are suitable for real-world IVS applications, and supports the results previously presented in May et al. [2008a], which were based on synthetic examples that were used to develop and evaluate the novel PMIS termination criteria.

6.4.2 Comparison of developmental frameworks

Current methods for ANN development require trial-and-error procedures to construct an optimal ANN model. In the approach presented in this paper, the IVS procedure yields an optimal model through statistical analysis of the input-output relationships that exist within the data. In the example given, ANN models were developed for a specific water distribution system, without the need for a priori expert knowledge or heuristics. Even where the input variables selected are consistent with previous approaches, the methodology is based on analysis of the data, rather than on heuristics, and thus provides a more rigorous basis for the inclusion of input variables.

The importance of a consistent, data analysis-oriented framework for ANN development becomes more apparent when considering the future application of ANN models to more complex water distribution systems. The relatively simple case studies considered thus far involved up to 500 candidate variables. For larger systems, the number of variables to consider could quickly increase to the order of 1 000 as the number of available parameters and the number of lags increase. As the complexity of the water distribution systems under consideration increases, the decision of which variables to include as inputs will become less intuitive, and modellers will find algorithms such as PMIS to be of immense value.

6.4.3 Interpretability of forecasting models

A perceived shortcoming of the ANN modelling approach is that the forecasts generated by an ANN model are somewhat inexplicable. Although an ANN model is able to generate accurate forecasts, Serodes et al. [2001] state that “...owing to its black-box nature, the results obtained cannot be explained.” The lack of interpretability is not surprising, since current methods for ANN development are somewhat holistic in that they do not consider the contribution of individual input variables to the model. However, from the results of the IVS implemented during model development using PMIS, it is apparent that the ANN can provide efficient and accurate predictions based on specific relationships that are identified within the data.

A review of the selected input variables can provide a simple, qualitative analysis of the specific patterns that are identified within the data by the IVS algorithm, and are then able to be used by the ANN to generate predictions. Water distribution systems are known to exhibit a strong periodicity due to diurnal patterns in demand, which are a major contributing factor in observed water quality behaviour [Polycarpou et al., 2002]. Periodic behaviour was evident in this case study, as observed for
the chlorine time-series shown in Fig. 4.10. It would appear, based on the input variables selected, that 24-hour cyclic behaviour is an important component within the data. For example, consider the input variables selected, which included past values of the output at time \( t, t-24, \) and \( t-47 \). The result is consistent with the notion of tendency in periodic, or oscillatory systems that has been defined elsewhere for similar forecasting applications where trends exist over homologous observations within the period of oscillation [Santos et al., 2005]. The selection of sequences of endogenous variables (e.g. \( C_{WDS} \) at time \( t, t-1, \) and \( t-3 \)) suggests that the current state, and immediate rate of change of the system, are also necessary for prediction. Interestingly, a similar pairing of endogenous variables at \( t-24 \) and \( t-27 \) was also selected as input variables, which suggests further reinforcement of short-term behaviour due to the 24-hour periodicity of the system.

Further insight regarding the mechanisms by which the forecasts are generated could be gained by a more quantitative method, such as sensitivity analysis of the models post-development. However, information regarding the importance of each input variable can be inferred based on the statistical measurement of input-output strength that forms the basis of the IVS approach. A measure of relative importance (RI) has been proposed based on analysis of the PMI for individual input variables [Soofi and Retzer, 2003], and which has been found to give results that are in good agreement with methods based on analysis of the trained ANN [Kingston, 2006]. The RI is determined directly from the PMI by the expression

\[
RI_i = \frac{I'_{C \cdot Y \cdot X}}{\sum_{j=1}^{n} I'_{C_j \cdot Y \cdot X}} \times 100
\]

where \( I'_{C \cdot Y \cdot X} \) is the PMI between candidate \( (C) \) and the output \( (Y) \), conditional on selected input variable set \( X \), which is estimated at each iteration of the PMIS algorithm.

The relative importance measures the relative contribution provided by each input variable, which indicates which relationships are likely to be predominantly used by the ANN model. The cost of monitoring and collecting data for a large number of variables can be a significant factor when evaluating the benefit-cost ratio of model development. A quantitative measure of RI is therefore useful in estimating the expected trade-off between model accuracy and the number of input variables used.

Based on the selected input variables in Table 4.2, it is apparent that the ANN developed is predominantly an auto-regressive time-series model, since it is dominated by endogenous lagged variables. The model is a highly accurate representation of the time-dynamics of water quality within the WDS, and as such can provide an early indication of downward trends in free chlorine residual that may warrant corrective action by the WTP operators. However, the PMI of applied chlorine dose, \( C_{WTP}(t) \) is relatively low, as is the PMI for residual at the FWS outlet \( C_{FWS}(t) \), indicating that only a weak statistical relationship was established between upstream and downstream chlorine. In the case of the data collected for the Myponga WDS, it is evident that the residual free chlorine data are simply too noisy, or the data contain insufficient variance to determine a relationship between applied dose and future downstream residual. This is likely, given the expected dampening of chlorine residual fluctuations over the span of the trunk main. Furthermore, it was not permissible to manipulate the chlorine injection rate, which meant that adjustments to the applied chlorine dose were typically small and infrequent, which resulted in the relatively low variability of chlorine residual within the system. It would be difficult to recommend use of the GRNN model to directly determine the influence of changes in applied dose. The development of control-oriented ANN models will need to consider other factors such as limited observability of the water distribution system (i.e. low variability of chlorination), noise, and process delays. In particular, due to the restricted scope for experimentation with disinfection parameters, the collection of operational data with sufficient variability for modelling chlorine disinfection presents a key area for future efforts, which should aim to define appropriate experimental protocols for undertaking WDS identification in a manner that ensures water quality is not compromised.
7 SUMMARY

Understanding water quality behaviour within water distribution systems is an essential requirement for effective water quality management, but is a less than trivial task because water quality behaviour is inherently complex. Predicting the quality of water at the customer tap is difficult for a number of reasons, including the non-linear dynamics of water demand, the heterogeneity of real-world pipe networks, and the uncertainty regarding the intrinsic chemical and biological processes mechanisms that drive water quality changes.

Modelling tools that have been developed to date are invariably of the extended period simulation (EPS) type. In this approach, a skeleton of a network is developed to represent all pipe, pump, tank and valve elements, which is used to simulate network hydraulics based on time-dependent demand. The hydraulic simulation can then be coupled to a time-dependent expression for water quality changes within the network to simulate water quality. EPS modelling is a relatively popular approach, and has been implemented in a variety of freely available and commercial software tools, which are used widely for system design and scenario analysis.

However, the EPS approach has some significant limitations. The requirement for extensive knowledge of the network including configuration and material properties, an accurate representation of water quality demands, and a suitable expression for water quality. Many simplifications and assumptions are often necessary, and so these models often fail to describe water quality behaviour with sufficient accuracy. Furthermore, simulation models require a significant amount of computational effort. While the amount of information generated is useful for system-wide analysis, this is often superfluous to the needs of applications that are only concerned with representing water quality input-output responses at critical control locations.

In moving towards a toolbox-oriented approach, an alternative modelling approach has been considered using statistical modelling tools. Statistical modelling considers the representation of water quality time-series or input-output responses based on a data-driven approach. In this case, the pragmatic aim is simply to identify a functional representation of the water quality changes over time, or between two locations within a WDS, that can be useful as a model. The advantage of this approach is that the behaviour described in the data can be represented as best as possible, by selecting a statistical model that optimally describes the data. There is no requirement for a conceptual understanding of the underlying processes that govern the WDS behaviour, and so this can be implemented with far less a priori knowledge.

Due to the acknowledged non-linearity of the relationships between water supply network parameters, this research project has focussed on the development of statistical forecasting models based on artificial neural network (ANN) techniques. The application of ANN models as a prediction/classification tool, or as part of an integrated modelling approach, is becoming more and more widespread, as their use continues to generate interest and gain acceptance within the water quality modelling community.

However, the flexibility of ANN modelling and analysis tools is both an advantage and a disadvantage, since there are potentially many choices that must be made during model development. Unfortunately, the “data-rich, knowledge-poor” circumstances that provide an opportunity to exploit the data-driven nature of the ANN modelling approach do not lend themselves to making reliable decisions based solely on judgement, which this has led to diversity of methods, and has slowed acceptance of ANN models.

Undoubtedly, there will be no single ANN development methodology that will best suit all possible applications, and in every model development some choices will need to be made. This research has investigated some of the core issues surrounding ANN model development, and has discussed the analysis that can be performed during model development to guide the modeller towards making good choices.
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