

## Development of a new analytical method for continuous on-line and *in-situ* monitoring in real world non-ideal environments

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### Extended Abstract

Reliable, continuous on-line water quality monitoring technology is becoming vital in the drive to ensure sustainable, safe supplies of freshwater resources in light of climate change, increased industrialisation and water scarcity (Schwarzenbach *et al* 2006; Diamond 2004; Allan *et al.* 2006). This is because currently, accurate and cost-effective on-line monitoring of various water quality parameters has proven difficult to achieve, as direct sensor deployment often means most sensors are unavoidably exposed to a wide range of varied and extreme measurement conditions (Diamond 2004; Allan *et al.* 2006, Frey and Sullivan 2004). The majority of on-line monitoring technologies currently employed are based on direct adaptations of traditional laboratory-based analytical methods, which were not originally designed for continuous or field based monitoring applications (Frey and Sullivan 2004; Danszer and Currie 1998). As the calibration models are based on Gauss's theory of least squares, they have the inherent flaw requiring strictly defined physicochemical measurement conditions in order to obtain quantitative results (Danszer and Currie 1998). This is because most sensors are not entirely selective towards one specific analyte and tend to suffer cross responses from the sample matrix. As ideal measurement conditions are rarely present in the natural environment, this invalidates the operating conditions required for reliable performance and hence leads to measurement errors. Consequently, these methods require frequent calibration, maintenance, complicated sample pre-treatment and consume large quantities of reagents in order to try and maintain their reliable performance (Frey and Sullivan 2004). However, the cost associated with maintaining instruments based on this measurement principle has greatly reduced their wide spread application, especially for remote, large-scale environmental water quality monitoring in places like the European Union (Allan *et al.* 2006). Therefore, simple methods that can improve the reliability, accuracy and economic costs associated with on-line monitoring such as maintenance and reagent consumption would be of great benefit to industry, government and research organisations.

The aim of this research was to develop a generic new analytical method specifically developed for continuous on-line monitoring in a diversified range of non-ideal

measurement conditions. This is becoming increasingly important as we produce potable water from more impaired or novel water resources and ensure that traditional water resources such as rivers and catchments are not contaminated. Hence in this paper we present a new analytical method that can enable a traditional laboratory-based sensor to intelligently respond *in-situ* to its measurement environment, negating the need for conventional calibration, reagents, sample pre-treatment or strictly controlled measurement conditions.

## Overview of New Analytical Method

The traditional water quality monitoring sensors are environmentally configured using a set of synthetic samples in the laboratory using a combination of hardware and software so that they are capable of acquiring quantitative measurements irrespective of measurement conditions. A traditional water quality monitoring sensor is defined as a sensor that is capable of selectively responding to the target analyte. They are capable of providing quantitative or semi-quantitative information with a certain degree of selectivity, provided strictly controlled measurement conditions are maintained. The new method employs a set of *in situ* matrix recognition sensors (MRS) to instruct the traditional sensor how to respond to dynamic non-ideal sample matrix conditions, by employing a backpropagating neural network algorithm. Matrix recognition sensors (MRSs) are defined as sensors that are capable of acquiring physicochemical information pertaining to the sample matrix. They include temperature, pH, conductivity, turbidity, Oxidation Reduction Potential (ORP), dissolved oxygen, in addition to optical sensors. However, the selection of appropriate MRSs will depend on the selectivity and known interferences of the selective sensor employed. The sensor is environmentally configured to a set of *in situ* MRS sensors to characterise its collective response to a set of prescribed non-ideal measurement conditions. A backpropogating neural network<sup>17</sup>, employing a supervised learning technique and sigmoidal squashing function was employed to used instruct the selective sensor how the collective matrix interferences denoted by  $\delta$  for a given set of prescribed non-ideal measurements affect raw signal response, with the non-linear and linear relationships being stored in the connection weights of the trained neural network. Once the traditional water quality monitoring sensor is environmentally configured, it is capable of autonomously and intelligently responding to its environment *in situ*. The data once captured is simply pre-processed and inputted into the trained neural network algorithm specific for each water quality parameter and the output (quantitative concentration) can be determined within seconds.

The method was demonstrated on a pH, fluoride, ammonia and ammonium sensor however, only the pH and fluoride are shown in this paper.

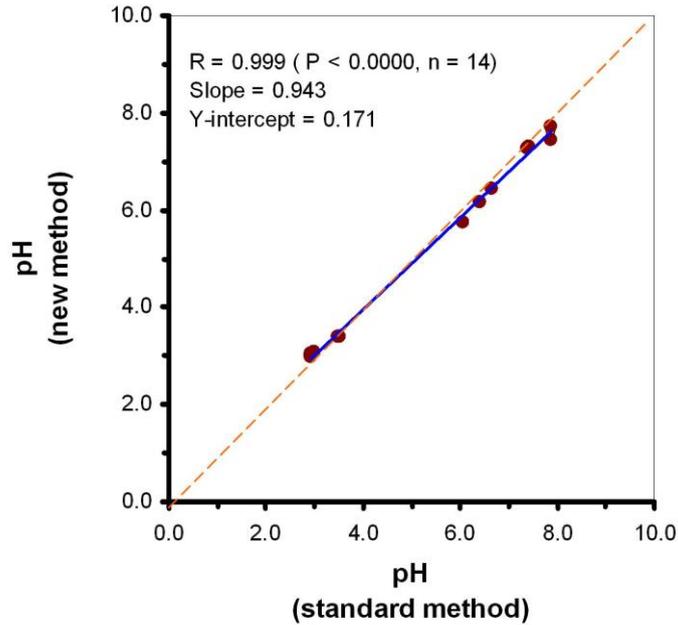


Figure 1 Shows the method comparison between a pH sensor measured using the standard method and environmentally configured pH sensor using real samples. The dashed line indicates  $y = x$ .

Figure 1 show the results obtained when a conventional pH sensor was environmentally configured employing the proposed method. 14 different water and beverage samples were analysed. Interestingly, the environmentally configured pH sensor produced quantitative results equivalent to the standard methods, as a correlation of 0.999 ( $p < 0.000$ ,  $n = 14$ ), slope of 0.943, y-intercept of 0.171, indicating  $y = x$ . Once environmentally configured, the pH electrode was capable of accurately determining the pH of a variety of synthetic and real samples over a range of 5 to 55°C, negating the need for conventional calibration or fixed measurement conditions.

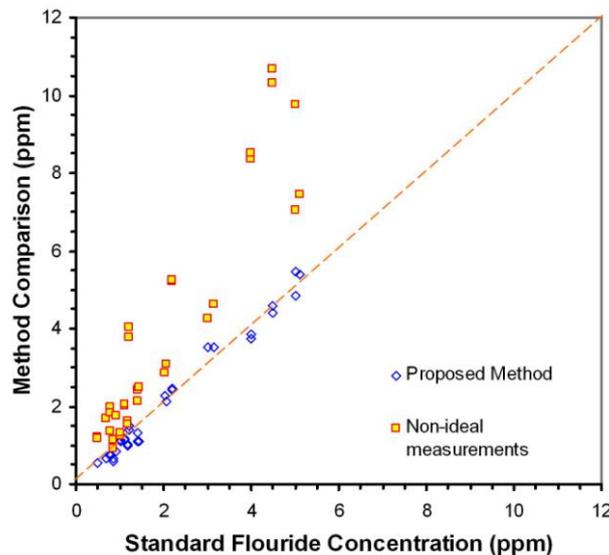


Figure 2 Shows method validation results between the new method and standard fluoride methods using three way method comparison on 33 (real samples from around Australia and synthetic samples). (◇) new method when measured in uncontrolled non-ideal conditions; (◻) non-ideal measurements.

When a conventional fluoride electrode is measured in non-ideal conditions. Both methods are referenced against the Standard method in controlled conditions (x-axis). The dashed line represents the method comparison line when  $y = x$ .

Figure 2 shows an example of the proposed method when it was applied to a conventional fluoride electrode. Currently, commercially available on-line analysers employing a fluoride electrode require calibration with standard reagents, temperature control and samples to be pre-treated with Ionic strength adjustment buffer to control pH and ionic strength. However, when the fluoride electrode was environmentally configured with a set of *in-situ* MRS, it was capable of intelligently responding to its environment, negating the need for strictly controlled physicochemical conditions, reagents, sample pre-treatment and calibration. This was evidenced by a correlation of 0.992 ( $p < 0.000$ ,  $n = 33$ ), slope of 1.05 and y-intercept of -0.06 with the standard method, indicating  $y = x$  ( $\circ$ ). When the same fluoride electrode was measured in uncontrolled conditions without employing the environmental configuration method ( $\diamond$ ), a correlation of 0.934 ( $p < 0.000$ ,  $n = 33$ ), slope of 2.06 and y-intercept of -0.384, was obtained with the standard method, highlighting there was significant error in the measurements as  $y \neq x$ . Uncontrolled measurement conditions refer to when measurements are performed without sample pre-treatment, calibration or fixed backgrounds.

Although the typical cost of ownership for a standard on-line analyser such as fluoride Ion Selective Electrode can range between \$5000 - \$15000, it is the on-going cost of maintenance pertaining to e.g. calibration and its reliability in the field that has greatly limited their widespread application. For example, according to two Australian Water Utilities, the cost of maintaining one on-line analysers such as fluoride or nutrient that require *ex-situ* calibration and maintenance is:

|  |                          |
|--|--------------------------|
| Vehicle Costs (< 3 hours travel time):         | \$15000 per annum        |
| Employee Salary Costs:                         | \$ 12480 per annum       |
| Reagents for calibration/sample pre-treatment: | \$1000-\$2000 per annum. |

Therefore, employing more reliable and simple to use on-line technology that negates the need for maintenance and standard reagents can produce cost savings for Australian conditions of approximating \$30 000 per annum per analyser. However, the greatest costs savings for these water utility would be having more reliable analysers for water quality compliance and process control. For example, for fluoride dosing it can reduce the reagent consumption consumed for a 180 ML/day water treatment facility by \$178 000 per annum, simply by improving dosing accuracy. In addition there are also other costs benefits associated with improved reliability and accuracy for water and wastewater treatment facilities such as by reducing the possibility of a false negative or positive event.

The results highlight the benefits of the proposed method for continuous on-line or field applications, as the sensors are configured to intelligently respond *in-situ* to their measurement environments whilst still being capable of quantitative measurements in uncontrolled conditions. As the method negates the need for conventional reagents, sample pre-treatment or calibration, it does not create secondary forms of pollution that require pollution, it is environmentally benign analytical approach. In addition,

this can significantly reduce the costs associated with maintenance, whilst improving accuracy.

**Acknowledgements:** I would like to thank the Co-operative Research Centre For Water Quality and Treatment and Griffith University for funding this project. In addition would also like to acknowledge the support/contribution of advisor Dr Chris Brown to the project.

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