CHOOSING THE RIGHT ONLINE FLUORIDE ANALYSER

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ABSTRACT

Beginning in 2003 Goulburn Valley Water (GVW) undertook a project to select preferred online instrumentation, in an attempt to identify which analysers are the right equipment for the right application. From this project several analysers were chosen as a suitable equipment application for the online measurement of Turbidity, pH, Chlorine, EC, Streaming Current and Fluoride. In 2007 GVW concluded that there were too many choices of analyser, and a preferred list was decided on to reduce the selection to just two of each group of analyser. The following paper reviews a trial of four online analysers for the measurement of Fluoride at the Shepparton Water Treatment Plant. From the trial, two meters were to be chosen as the best fit application for the preferred list. This paper also seeks out to answer the question on the need to have Total Ionic Strength Adjustment Buffer (TISAB) as an online reagent or not. The need for such a trial was highlighted as GVW at the time were undertaking tendering for three new fluoride dosing plants, and the selection of an analyser is critical to its operation. Overarching all of this process was the release of the new code of practice for fluoridation by the Department of Human Services, Victoria.

1.0 INTRODUCTION

On-line instrumentation has become one of the most valuable tools in the operators arsenal in terms of providing "Safe" drinking water 100% of the time. It is for this reason due to their importance that they must be accurate and reliable, they must also be supported by reliable service and calibration. The calibration needs to be simple with the least amount of steps possible and not too time consuming. The instrument should be well supported by after sales service for spare parts and advice. Above all it must meet the new DHS Code of Practice on Fluoride under section 4.5 Process Control and Instrumentation.

The Code states that "*Dosing fluoride into drinking water is a continuous process that will involve lifetime exposure to fluoride for most consumers. It is therefore essential that the authority has in place a validated and verified system of accurately controlling fluoride dosing at all times*" to meet this, on-line instrumentation must be accurate and reliable. Accuracy in the code is clearly defined as "*The authority should carry out method and instrument validation to determine a limit of detection and resolution of their measuring instrument. Accuracy to at least +/- 0.15 mg/L should be achieved by a well-maintained instrument in a production environment"*.

2.0 ANALYSER SELECTION

With all of these factors in mind GVW undertook a trial to identify what instrument was the best fit to address accuracy, reliability, service, ease of calibration, parts availability, size and position, purchase and running costs.
Four separate suppliers were approached for the availability of a trial unit to compare and judge for ourselves the best fit unit that meets all the criteria stated above. The following suppliers and units where chosen:

- Orion Pacific, Orion Series 1800 Fluoride Analyser
- Prominent, Dulcometer D1C with fluoride sensor FLE 010 SE

- ABB, 8231 Fluoride meter
- Alldos, Conex multi fluoride meter

The rationale for choosing these meters was to compare two meters with online TISAB reagent addition and two without. The Orion and ABB were selected as the TISAB meters due to both being on our list of approved meters. The Prominent and Alldos units were chosen as non TISAB units due to presently using the Alldos and the popularity of other water authorities for the Prominent unit. As the Orion unit and Alldos units were already in operation Prominent and ABB were approached to supply the trial units. Both suppliers also brought and installed their units free of charge to ensure that the units would be at the optimum operation. All units were installed in the one room off the same sample line.

3.0 THE TRIAL

The trial was undertaken over 6 months in an attempt to pick up any difference between the four meters over varying flows, temperatures, plant operations and fluoride masking agents.

To compare the four units a 4-20 signal from the unit to SCADA was installed. Once the signals were connected a page was set up on SCADA to compare trending, (See Fig 1). Initially the Alldos unit was left out as it was still recording final water and needed to be kept online until one of the other units could replace it for the purpose of the trial. To check accuracy of the on-line units samples were taken from the units to compare results using the method referred to in the DHS Fluoride code "*The authority must measure the total amount of fluoride in the supplied drinking water. The method for measuring the total fluoride concentration must conform to the ion selective method as described in the current edition of Standard methods for the examination of water and wastewater 4500-F-C". (See Table 2)*

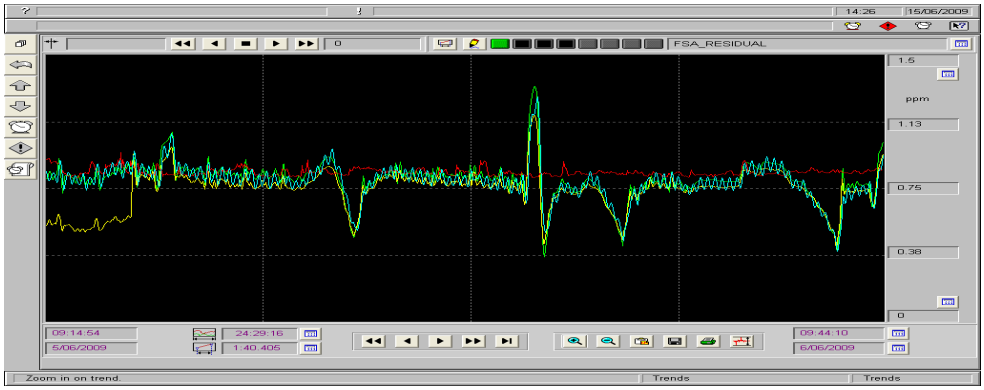

Figure 1: ***SCADA trend showing a uniform trend from the trial meters. Note the yellow line of the prominent analyser before and after a calibration.***

This also assisted identify differences between the TISAB and Non TISAB meter results or referenced interferences. At varying times during the trial, suppliers came and serviced the on-line units to ensure that the meters were still performing at their peak performance. Calibrations were performed on intervals recommended by the suppliers, by GVW staff to ensure ease of calibration from an operators perspective was correctly recorded.

4.0 THE MEASUREMENT OF PERFORMANCE

To compare the performance of the meters a measurement Scorecard was introduced to try and independently measure the optimum meter for GVW needs.

The scorecard points system is, 1 is not acceptable to 5 which is excellent . These score where decided on in consultation with operations and water quality departments to ensure objectivity

In the cases of price and accuracy the points system is straight forward but in terms of maintenance and service it is purely the general feeling of the panel member based on contact with the supplier.

For the purpose of this paper we will look at each unit individually and then the combined scores to evaluate the best unit and in no special order.

Table 1: ***Scorecard***

Category	Orion	ABB	Prominent	Alldos	Rank
Accuracy	5	5	5	5	All rank 1st
Reliability	2	4	5	4	Prominent
Service	2	5	4	4	ABB
Ease of Calibration	1	5	4	4	ABB
Parts availability	2	4	5	4	Prominent
Size and Position	2	2	4	5	Alldos
Costs	2	2	4	5	Alldos
Results	**15**	**26**	**31**	**31**	Alldos /Prominent

5.0 THE SCORING BREAKDOWN

5.1 Accuracy

Using the DHS guidelines under *The method for measuring the total fluoride concentration must conform to the ion selective method as described in the current edition of Standard methods for the examination of water and wastewater 4500-F-C".*

Using this method to carryout bench top testing to verify accuracy of each meter to be within the recommended *+/- 0.15 mg/L* all analysers were found to be within this range and as can be see by Table 2 most results were within +/- 0.1mg/L so all meters scored the maximum 5 points.
This was repeated at least once a fortnight for 4 hrs during the trial and each time the results were repeatable.

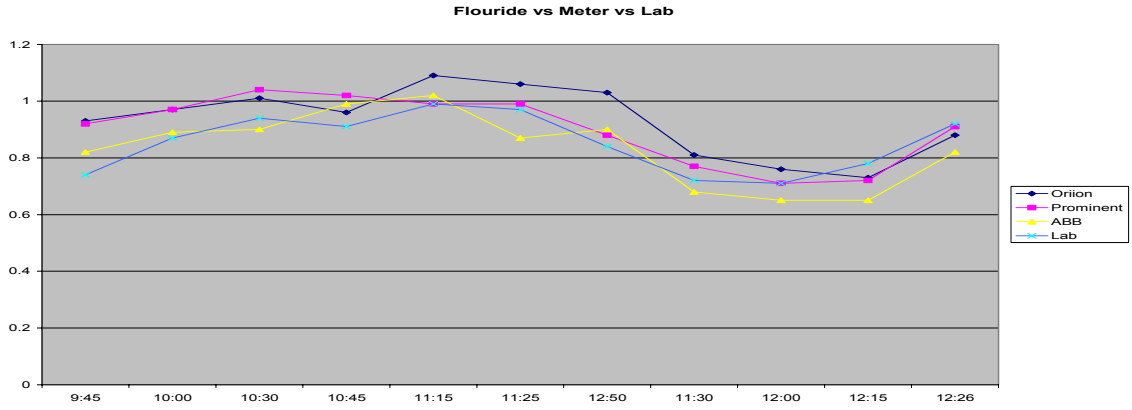

Figure 2: ***Bench top vs online analysers***

5.2 Reliability

As the trial period was only undertaken for 6 months reliability can only be discussed for that period on the Prominent and the ABB which did not falter in that time. Whereas the Alldos and the Orion have been inline for more than a year at the Shepparton plant and a bigger maintenance picture has been constructed. In that time it has been identified that the Alldos analyser requires the need to change the probe at least once per year. After two years of running a card fault appeared but was rectified quite easily by our in house Instrument Technician. The Orion in comparison looks to require a fluoride and reference probe change every six months, other failures include changing of the small peristaltic pump, inline filter blockages and card failure that required replacing. The Prominent comes out on top purely because of the limited amount of parts to that could fail compared to the ABB but only time would tell if this was the case.

5.3 Service

ABB come out on top for service but very closely followed by Alldos and Prominent. This is not only based on the experience of these analysers but also from previous dealings with all four suppliers over several years. ABB went above and beyond to ensure their unit was operating at its peak at all times with many backup visits, whereas Prominent and Alldos helped with the installation and back up call support as well as onsite help when asked. Orion on the other hand will only deal over the phone as they are based in Sydney.

5.4 Ease of Calibration

ABB again come out on top with their unit have an automatic calibration system that utilises to online standards of 0.2 and 2.0. This calibration can be set to run at any time period and the application at Shepparton worked on a calibration every third day.

This system was well received by the operators who agreed the changing of the standards once a month was acceptable. The Prominent came in close behind as did the Alldos as both calibrate similar to present online Chlorine analysers within GVW.
The Orion procedure is lengthy and requires very close attention which for a novice can take up to an hour to ensure correct calibration.

5.5 Parts Availability

Under section 7 Reporting and Auditing on Table 4: Emergency and exceptional notifications of the DHS code of practice, water corporations are required to report to DHS within 24hrs if *Fluoride dosing is less than the lower action process limit for a continuous period of >72 hours.* Due to this requirement availability of parts is critical to the analysers operation and Prominent come out on top due to availability of parts and support can be sourced in a short time frame.
Alldos came in close behind except they use a Orion fluoride probe and are subject to lengthy periods in response from Orion, but they do keep some in stock. ABB are also very good but their unit may require an ABB tech as units such as the heating block may require a more specialist input.

5.6 Size and Position

Both the Alldos and Prominent feature well here as both are small units in comparison to the ABB and Orion (see Figure 3).
The Alldos unit is the smallest by far and is very easy to install. The ABB and Orion units look to be affected by ambient temperature and prefer to be installed in a room with a constant temperature of around 20 to 25 degs.

Figure 3: ***Orion, Prominent and ABB units***

5.7 Purchase and Running Costs

The Alldos and Prominent units can be purchased under $10, 000 each whereas the Orion and ABB units have price tags above the $20,000 range. Added to this the ongoing cost of online TISAB at $1800 a box (20L), times three times a year makes both these units a costly piece of equipment. All four units appear to require their probes to be changes yearly and so the service costs are similar. As the Alldos unit is basically a probe in water it is the cheapest by far in relation to running costs.

6.0 INTERFERENCE TO A QUALITY RESULT

It must be pointed out at this part of the paper that the selection of a fluoride meter is for the purpose of an analyser for GVW and its needs and not a recommendation of a one size fits all meter for all water authorities. This is just as relevant when it comes to a fluoride analyser due to chemical compounds that can bind and mask the fluoride ion. Therefore the need for a meter that requires on-line TISAB to unbind the fluoride from compounds such as Aluminium, Iron and Calcium is a necessity. Levels of aluminium's higher than 3.0mg/l and Iron higher than 200mg/L each introduce an error of 0.1mg/L of the available fluoride at 1.0 mg/L. This is where units utilising TISAB become critical to accuracy. In the case of GVW's water at the Shepparton plant these levels are rarely seen and for the new installations at Cobram, Kyabram and Seymour it is even lower in trace levels as can be seen in Table 2. It can also be argued that if you have Aluminium's higher than 3.0 mg/L and Iron higher than 200mg/L you would be better off addressing your treatment problems before introducing fluoride. But at times of peak levels on-line TISAB could be your answer. Taking this into consideration added to the results from scorecard the Alldos and Prominent come out as the obvious choice as the preferred instrument for GVW's application. It clearly showed in the trial and as can be seen in

Figure 1 that the TISAB and the non TISAB meters recorded a very similar result and the use of TISAB was not showing a any apparent significant difference brought about by separating the masking compounds.

It was then decided to move on to show what the difference between the Alldos and the Prominent meters might be considering that the Prominent uses a pH compensation inline with the fluoride probe whereas the Alldos works on the principle that the pH of the water is between 6.5 and 8.5 and therefore no change in the fluoride result would be seen as stated in the *Standard methods for the examination of water and wastewater* 4500-F-C state that the fluoride buffer (aka TISAB) is a mixture of CDTA, acetic acid, sodium hydroxide and sodium chloride and is prepared to a pH of 5.3 to 5.5.

The fluoride buffer is used to reduce the following interferences:

- CDTA preferentially complexes interfering cations and releases free fluoride ions
- In acid solution, F^- forms a HF complex but the buffer maintains a pH above 5 to minimise hydrogen fluoride complex formation
- In alkaline solution hydroxide ion also can interfere with electrode response to fluoride ion whenever the hydroxide ion concentration is greater than one-tenth the concentration of fluoride ion.

To investigate this issue both meters were again put online and the pH adjusted to check for drift between the two meters, particular at the higher pH values of 8.0+ (note the Orion was also still online as a comparison). No noticeable or strong conclusion could be drawn from this trial.

Table 2: ***Recorded levels of masking agents***

Town	Al (Acid Soluble) Ave (mg/L)	Al (Acid Soluble) Highest (mg/L)	Total Al Ave (mg/L)	Total Al Highest (mg/L)	Al Reactive Ave (mg/L)	Al Reactive Highest (mg/L)	Fe Ave (mg/L)	Fe Highest (mg/L)
Kyabram	0.04	0.79	0.04	0.12	0.02	0.16	0.02	0.14
Seymour	0.05	0.86	0.05	0.96	0.03	0.72	0.13	1.1
Cobram	0.03	0.16	0.03	0.04	0.03	0.14	0.02	0.05
Shepparton	0.05	0.34	0.05	0.4	0.02	0.15	0.03	0.17

7.0 CONCLUSIONS

Looking at the comparison of scores it is easy to see that the units without the TISAB rate higher and this is due to the purchase and running costs, as well as the ease of calibration. While the ABB had the easiest of calibration procedures, operators found the need for constant preparing of standards and filling a task they would do without, if the equivalent meter had a simple calibration procedure. The decision that TISAB was not required in our application was recommended and as the new sites would also not require the online addition, the choice was then between the Alldos and the Prominent analysers. The Alldos and Prominent come out in the scorecard on the same level and it is only the technical difference of pH compensation that separated the two. As pH plays a critical role in online fluoride measurement, the inclusion of the Prominent pH compensation for slight variation just piped the Alldos meter out as preferred fluoride analyser.

8.0 Acknowledgements

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