Complying to Regulatory Fluoridation Standards and selecting the best Fluoride Analyser

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Significant progress in refinement of chemical sensing techniques has enabled on-line monitors to be applied in many areas: monitoring and controlling waste water treatment, policing of discharges into the natural water courses and quality assurance in treatment of potable water. However, an understanding of their limitations is essential in ensuring the validity of the results obtained. A notable example is the monitoring and control of fluoride concentration.

When a fluoridation process is included in potable water treatment, strict monitoring and control is vital to ensure that the regulatory 1 ppm, or 1 mg/litre, concentration is maintained. The widely accepted fluoride ion selective electrode is an attractive candidate for implementing such control. However, the highly reactive nature of the fluoride ion, can in certain areas, pose problems which can seriously jeopardise valid measurement and risk regulatory non-compliance. In addition, choosing the wrong technology can mean high operating and maintenance costs that can increase excessively over the life of the asset.

Conventional ion-selective electrodes for Fluoride measurement based on lanthanum fluoride crystal will only respond to free, or ‘unbound’, fluoride ions. Many conditions present in natural and treated waters will influence this free Fluoride concentration. For example, at low pH the presence of certain metal ions and temperature can change the proportion of fluoride ions complexed, or ‘bound up’, thus rendering them ‘invisible’ to the electrode.

In addition, the stronger the fluoride complex formed, the greater the proportion of free fluoride ions complexed and the sample measurement will become less reliable. In a sample at pH 5.5 the fluoride content will be free and therefore detectable by the fluoride electrode.

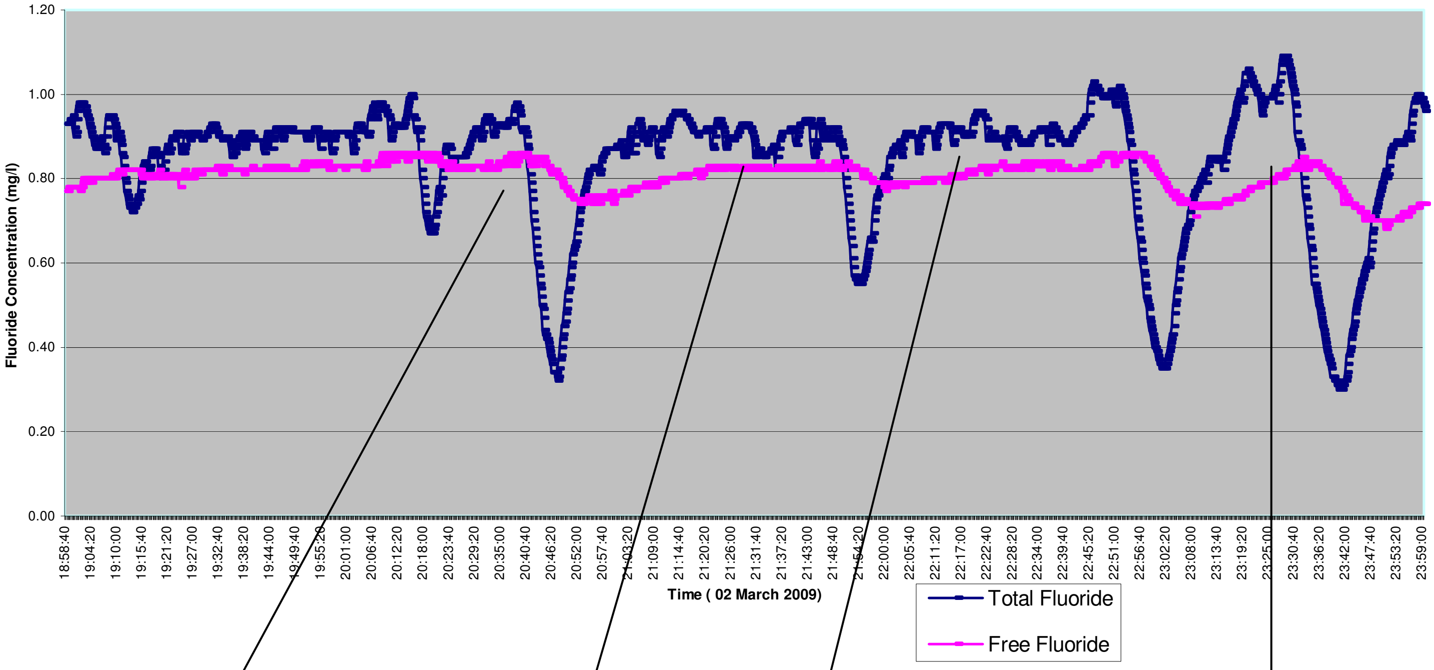
However as the pH moves to lower levels, the portion of fluoride ions complexed as HF, ‘unseen’ by the electrode increases rapidly. At pH 4.5 more than 5% of the fluoride content becomes bound up and at pH 3.2 only 50% remains free. Such fluctuations in pH occur frequently in unbuffered waters.

Small concentrations of iron or aluminium can have an even more dramatic effect. In the coagulation stage of the water treatment process, iron or aluminium sulphate may be used as a coagulant. The residual aluminium or iron in the water, following settlement and filtration, may only be a few ppm but will bind fluoride in a series of complexes to which the fluoride electrode will not respond. Being trivalent ions, each iron or aluminium ion has the potential to bind six fluoride ions. Similar effects will be caused by the presence of calcium or magnesium.

In practice, however, it is often difficult to specify precisely the nature of samples so that confidence can be placed in basic monitoring packages, like Free Fluoride Analyzers, which only respond to ‘unbounded’ fluoride. Furthermore, the constraints placed on fluoride dosing control, including varying Fluoride chemical strengths, make it inappropriate to rely on guesswork or incomplete information when complying with legislative requirements and ensures optimum cost control of dosing process.

The presence of this **‘hidden fluoride’** can be clearly seen below, where a Total Fluoride Analyzer was trialed against a Free Fluoride Analyzer.

Fluoride Measurement - Total Vs Free - WTP, Vic Australia



Trends in Fluoride concentration not detected by Free Fluoride Analyser

Generally higher total Fluoride measurement value compared to Free Fluoride measurement, indication of the presence Fe, Al, Ca and other components which often vary in concentration

Faster and accurate response to changing Fluoride concentration from Total Fluoride Analyser

High dosing concentration not picked up by Free Fluoride Analyser, while Total Fluoride Analyser has detected the excess dosing

The complexities involved in maintaining accurate levels of fluoride concentration are clearly documented. **The Code of Practice for Fluoridation of Public Water Supplies- [Act 1957], issued by Department of Health- NSW [2002],** for example, covers technical aspects of fluoridation of water supplies in NSW, and reinforces the issues of maintaining fluoride concentration in water supplied at **1.0 mg/litre** and using **appropriate total ionic strength adjusters {TISIB reagents} to measure ‘total’ Fluoride [Clause 9.2.13]**.

Under the Code’s operational criteria, to ensure that the legislative fluoride concentration is maintained at, or soon after, the point of injection, fluoridation plants are required to **operate between 0.9 and 1.5 mg/litre** for at **least 95%** of the plant operation time. It should not however **exceed 1.5 mg/litre**.

Similar codes are enforced throughout other Australian States and Territories.

To monitor and control Fluoride at these levels, and overcome the issue of undetectable complexed fluoride ions, it is imperative to have a **Total Fluoride Analyser**. This will assist plant operators meet their legislative requirements, while offering tighter control of their dosing process to minimize costs.

Total Fluoride Analyzer controls the sample conditions before measurements are made. The monitor continuously adjusts the pH and temperature of the sample, as well as introducing a reagent solution to 'free up' fluoride ions complexed by interfering ions. In this way, measurements and calibrations are made under standard conditions, thus optimising validity.

As well as providing a reliable fluoride monitoring service, the analyser can also be used to carry out certain control functions. As a known amount of water flows through the works, a dosing pump is used to add fluoride to achieve correct concentration. Bulk concentration is controlled by pump speed adjustment from flow rate signals. The fluoride monitor will feed back information which, if necessary, will be used to adjust the stroke of the dosing pump to maintain precisely the 1ppm concentration level required.

When selecting a Total Fluoride Analyser it is prudent to review the liquid handling section to ensure minimal routine maintenance and on-going operational costs. Advances in technology now enable features such as **automatic two-point calibration**, **reagent level detection and remote diagnostics** to assess the sensor's performance as well as a **constant temperature cell** to eliminate temperature variations.

On-going life cycle costs can be minimised through eliminating manual operator lead calibrations, using pre-prepared reagents rather than preparing on site, and choosing analysers that are simple to set up and use.

In summary to ensure compliance to Fluoridation Regulatory Standards, and to select the right Analyser, the following needs to be considered:

- Measurement of **Total Fluoride** through the use of Total Ionics Strength adjuster reagents.
- **Total Fluoride Analysers that have a constant temperature cell** eliminates Fluoride measurements variation due to ambient and process temperature changes.
- **Automatic two point calibration** ensures more reliable and accurate measurements compared to manual calibration techniques. Simple pre-configured auto calibration feature eliminates the need for an operator to perform manual calibration, saving money and manpower in addition to reducing safety concerns associated with chemical handling.
- **Remote Diagnostics**, such as the ability of Analysers to indicate when reagents require replenishment, is particularly useful in remote sites.

- **Provision of pre-mixed reagents** that will enable greater confidence in the quality and consistency of reagents while eliminating the requirement for operators to prepare their own reagents.
- Simple to use Analysers that have set maintenance intervals with well-established **local Service Centres**.

For further information on Fluoride Analyser requirements please contact your ABB representative.

www.abb.com/analytical
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