FLUORIDE LABORATORY TEST METHOD CHALLENGES AT WANGARTTA WTP

Paper Presented by:

Kriston Nilsson

Author:

Kriston Nilsson, *Water Treatment Operator*,

North East Water

71st Annual Water Industry Engineers and Operators' Conference
Bendigo Exhibition Centre
2 to 4 September, 2008

FLUORIDE LABORATORY TEST METHOD CHALLENGES AT WANGARTTA WTP

Kriston Nilsson, *Water Treatment Operator*, North East Water

ABSTRACT

North East Water (N.E.W.) commenced dosing fluorosilicic acid into the Wangaratta and Wodonga town water supplies, in August 2007. The SPADNS colour metric method (0.02 to 2.00 mg/L F^-) was initially selected to validate mass balance calculations for dosing fluorosilicic acid. Inconsistent laboratory results for the SPADNS test method occurred at the Wangaratta Treatment Plant, however not at the Wodonga Treatment Plant. The inconsistencies were investigated with temperature and water matrix interference being the likely causes. NEW has since purchased Ion Selective Electrode test equipment that has generated accurate results for Wangaratta treatment plant.

This paper focuses on investigation and actions taken to produce reliable Fluoride test results at the Wangaratta water treatment plant.

KEY WORDS

North East Water (NEW), Mass Balance (MB), Trisodium (4,5-Dihydroxy-3-[(p-sulfophenyl)-2,7-) naphthalenedisulfonic Acid (SPADNS), Ion selective Electrode (ISE), Total Ionic Strength Adjustment Buffer (TISAB), Fluorosilicic acid (FSA)

1.0 INTRODUCTION

North East Water (N.E.W.) commissioned a FSA dosing plant at Wangaratta in August 07. MB calculations manage the system, with the daily SPADNS test and in-line analyser used to verify F^- concentrations. Weekly testing was completed by both NEW and an external laboratory service.

The SPADANS test is an inverse colorimetric reaction (range of 0.02 to 2.00mg/L F^-). As spectrophotometers were on hand, SPADNS was the preferred method. Duplicate samples and a 1-ppm standard were tested for proficiency purposes following the correct reaction procedures.

The results obtained in Wangaratta showed inconsistencies between MB calculations, external laboratory service and the regularly NEW SPADNS testing. Operations staff became less confident in the testing procedure leading to further investigation.

Literature investigation suggested research into an ISE was necessary. ISE testing measures ion activity over the probe face. The addition of TISAB buffer solution creates a uniform ionic strength background, adjusts pH and breaks up F^- complexes to restrict interferences.

2.0 DISCUSSION

2.1 Data

Text research identified error margins with the SPADNS method, a sample of F^- was tested in 53 laboratories and the results gave an average relative error of ± 1.2% Mary

Ann H. Franson; M; 1992.
This error would cause a 1ppm sample to produce a result between 1.012ppm and 0.988ppm. The range suggested could not resolve the irregularly results.

2.2 Sample Temperatures

SPADNS suppliers and text methodologies advised the sample and blank to be within ±1 degree Celsius. During colder month's temperature differences between external samples and internally stored blank water increased to approximately six degrees.

To maintain a constant laboratory temperature a reverse cycle air conditioner was installed. This insured a constant Temperature of 23^{oc} in the laboratory. No effect was observed as the temperature differential between the external samples and blank was still present.

The initial trial involved immersing vials containing blank, sample and standard into hot water baths. Hot water was used to decrease the equalization time, therefore reducing possible fluoride glass etching. Raising the temperature above standard laboratory reaction temperature increasing the reaction rate negatively affecting the results.

The second trial involved equalizing the blank under a flowing sample tap. Equalizing the blank as an alternative to the sample reduced possible glass etching. Once equalized 10ml of sample was tested. This process had a positive affect reducing the error. The preparation required extended periods of time and become inefficient.

2.3 Result Replication

Samples tested during commissioning were duplicated for proficiency reasons, one blank and two samples. The duplicated samples regularly produced repeatable results, therefore yielding a double false or correct result.

2.4 Sensitivity of Volumes

Volumetric error was considered to potentially be contributing to the irregular results. An Automatic pipette was calibrated having little effect on the results. Researched texts suggest, "Volumetric measurement of sample and reagent is extremely important to analytical accuracy" when using the SPADNS methodology Mary Ann H. Franson; M; 1992. Error review was completed showing the minimum mass of the calibration scales was 0.001g allowing for a ± 0.001ml difference. The pipette has an accuracy of ±0.25%, therefore ± 0.0125ml in the 5ml sample. Adding the errors a total of ±0.026ml in each 10ml sample could occur. This error would affect duplicate samples, whether correct or incorrect they were comparable. Volumetric differences were negligible, duplicated samples gave comparable results suggesting very minimal effect of volume errors on final results.

2.5 Sensitivity of Time

The SPADNS test requires one-minute reaction time and the change is virtually instantaneous. The examination of reaction time versus results showed no variation. If the SPADNS reaction was time critical the second duplicate sample would register constantly different results and this did not occur.

2.6 Glassware

Glassware interference was considered as a possible negative effect on results. Three new vials were rotated to identify any changes. Minimal variations occurred discounting the glassware effect.

2.7 Changing flows and Probe Reactivity

Wangaratta WTP has varying final water flows that require the FSA to be flow paced. In-line probe display versus true concentration can vary due to the probes reactivity. This was considered during commissioning, therefore only samples taken during consistent flow periods were considered for a reference.

2.8 Interference

Known chemical interference's to the SPADNS test are higher than potable water quality limits. Aluminum's (Al^{3+}) interfering concentration was 0.1mg/L and only reduced the fluoride result by 0.1mg/L Mary Ann H. Franson; M; 1992. Wangaratta WTP regularly produced Al^{3+} 0.006mg/L. Interference from chemical substances not listed could be related to the irregular results.

During colder months the irregular results increased. A hypothesis suggesting storm water runoff or a chemical more detectable in colder samples may affect the results. The suggestion of unknown substances causing irregular results requires research above and beyond this paper.

2.9 Proving Ion Selective Electrode

Once the options were examined, NEW decided to purchase an ISE. Throughout commissioning, MB and the external contractor testing (using an ISE) regularly produced higher results than NEW SPADNS results. ISE analysis demonstrated no irregular results and closer correlation between the MB, external testing and inline Ion selective electrode.

2.10 Data Comparison

The results gained using the external contractor and NEW's ISE were more similar than with the SPADNS results. Shown below is the percentage difference between results gained from NEW ISE and SPADNS and the external tester's ISE.

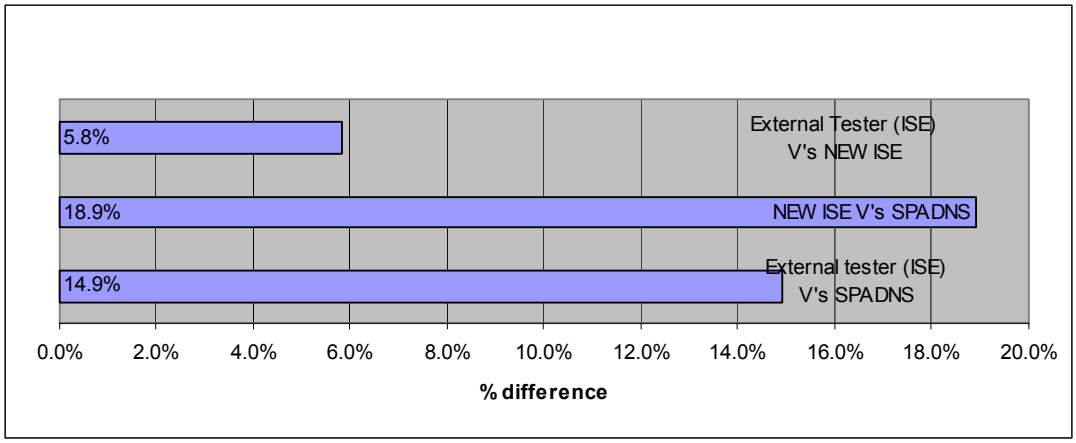

Figure 1: ***Percentage Difference Between Testing Methods***

The SPADNS relative error of ± 1.2% is greater than ±0.7% of the ISE. Calculated out, a 0.8ppm sample would read 0.7712mg/L and 0.736mg/L for the ISE and SPADNS respectively Mary Ann H. Franson; M; 1992. The relative errors shown graphically below suggest the ISE has less variation than that of the SPADNS test.

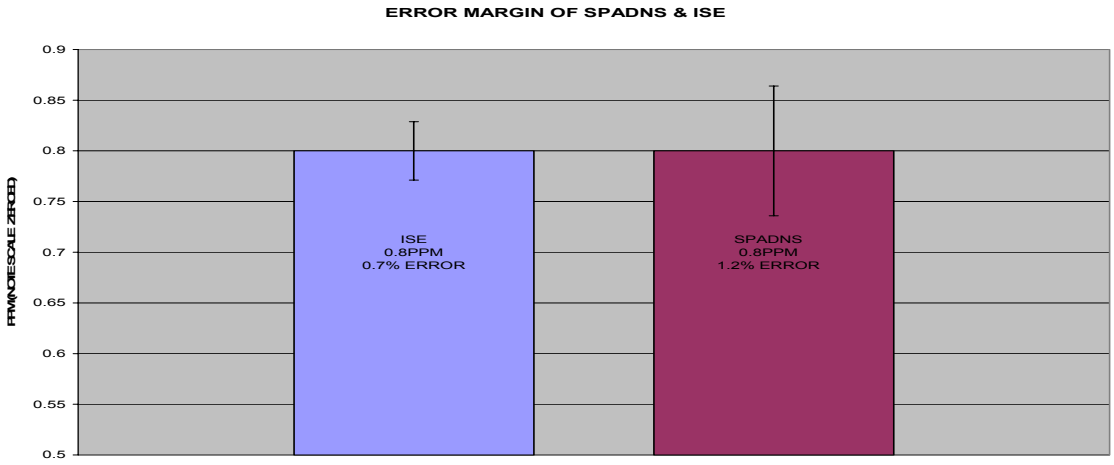

Figure 2: ***Error Margins of ISE & SPADNS Testing Methods*****, (Mary Ann H. Franson; M; 1992)**

2.11 Practicality

A notable disadvantage of SPADNS is the dark red reagent, staining benches and glassware. TISAB used for ISE is a clear solution, less problematic in the laboratory. OHS issues can arise with SPADNS reagents being corrosive, causing burns to bare skin and eyes. TISAB is non hazardous, only requiring local first aid if contact occurs.

3.0 CONCLUSION

The results and operator preference suggested the Ion Selective Electrode was more robust and user friendly. Possible causes of irregular results from the SPADNS method were explored without a proven outcome. Irregular results continued after the method verification, an unknown interference or temperature hyposensitivity was hypothesized as the cause. The Ion selective electrode is still used at the Wangaratta WTP. As fluorosilicic acid dosing plants are constructed within North East Water, Ion Selective

Electrode's will be purchased. The main reason is the usability and robust results produced in field and laboratory applications.

4.0 ACKNOWLEDGEMENT

Thanks to the Wangaratta treatment team for their assistance, data collection & paper reviews.

5.0 REFERENCE

Mary Ann H. Franson; M; 1992;*Standard Methods 18th edition 1992 For The Examination Of Water And Wastewater* ; Fluoride (4500- F^-)/ Preliminary Distillation; pg 4-59 to 4-64;Americal Public Health Association; Washington DC.