**Fluoride Detection and Removal in Drinking Water**

Student Name

Longwood Senior Thesis Proposal

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**Specific Aims**

In this project, fluoride levels found in drinking water will be analyzed. Several methods of removal and detection will be compared including ion-selective electrodes, cyanine dyes, alumina and carbon filters, in addition to an at-home test kit. The goal of this project is to evaluate methods that are less expensive or complicated than traditional methods and compare them to that of an ion-selective electrode.

**Introduction and Literature Review**

In the early 1900s, brown stains on the teeth of young Colorado residents caught the attention of Dr. Frederick McKay, a young dentist. He noticed that in severe cases, the teeth looked as if they were covered in chocolate. McKay partnered with a colleague, Dr. Green Vardiman Black, and in 1909 discovered that the mottled enamel was the result of developmental imperfections in children’s teeth and that children who had not developed their second set of teeth were at a higher risk. By 1915, Dr. Black had passed away but McKay discovered that the condition was related to the drinking water and the enamel in these teeth was incredibly strong. It wasn’t until 1931 that a chemist in Michigan working for ALCOA Aluminum company read the findings of Dr. McKay and connected it to one of his studies that they realized the cause of the mottled enamel was excessive fluoride in drinking water.[1]

ALCOA had charged their chief chemist, H. V. Churchill, with refuting claims that aluminum cookware was poisonous. This prompted him to test his water using photospectrographic analysis only to find that it was not the aluminum that was causing negative health effects in residents, but a high concentration of fluoride ions in the drinking water. These findings sparked an investigation led by Public Health Service scientists that would determine the effects of fluoride on tooth enamel. They developed methods to more accurately measure fluoride levels in water and used them to compare fluoride levels in drinking water around the country. Levels up to 1.0 ppm of fluoride ion in drinking water were determined safe for consumption because in most people it did not cause fluorosis but instead had the benefit of making their tooth enamel unusually resistant to decay.[1]

After many debates between PHS, the Michigan Department of Health, and other public health organizations, Grand Rapids, Michigan became the first city in the world to fluoridate drinking water in 1945. After 11 years, the caries rate or rate of decay and crumbling of teeth among children born after fluoride was added dropped more than 60 percent. This led to the fluoridation of water in cities across the country.[1] Today, more than 200 million Americans drink water with enough fluoride in it to prevent tooth decay. That equates to almost 75 percent of the people who drink from public water supplies.[2]

The issue that the residents of Colorado and Michigan faced was that there was too high of a concentration of fluoride in the water that caused staining of the teeth. This excess of fluoride that causes yellow or brown stains to form on teeth is called fluorosis.[3] Almost all water contains naturally occurring fluoride but usually, it is not enough to cause fluorosis. Most counties treat their water for a variety of contaminants which include methods of water fluoridation or the process of adjusting the level of fluoride in water.[2] However, there are still some rural counties in the United States that do not treat their water before it is pumped to residents.[4]

The World Health Organization established a fluoride standard for drinking water of 1.5 mg/L. This was due to the consumption of high levels of fluoride being linked to dental and skeletal fluorosis and the occurrence of fluoride contamination becoming prevalent across the world. These ailments are more detrimental to children because their dental enamel and skeletal formation are not complete. Concentrations of fluoride between 1.5 and 3.0 mg/L result in browning and mottling of teeth and further exposure leads to hard brittle teeth. Fluoride concentrations between 4.0 and 8.0 mg/L result in skeletal fluorosis which can develop into crippling fluorosis if the level exceeds 10 mg/L. Additionally, ingestion of high levels of fluoride can cause urinary tract malfunction, muscle fiber degeneration, gastrointestinal problems, red blood cell deformities, reduced immunity, and neurological manifestations.[5]

Natural sources of fluoride commonly arise from the dissolution of natural fluoride-bearing minerals like fluorspar, fluorapatite, amphiboles, hornblende, tremolite, and biotite. For example, reports from the district of Odisha state in India claim that 27 out of the 30 districts in this state that are contaminated by fluoride. It was inferred that the major source of fluoride in Odisha was weathered rocks.[6] In a study by Luo et al. performed in the Yuncheng Basin of China, it was found that the main source of fluoride in the groundwater was contamination from pesticides, fertilizers, and industrial waste discharge. Evaporation also plays a key role in the enrichment of fluoride through the removal of calcium. Desorption of fluoride from mineral/organic matter surfaces was enhanced under alkaline conditions and high bicarbonate ($HCO_3$) content in groundwater.[5]

One of the most common methods of detection for fluoride in water uses an ion-selective electrode (ISE). Ion-selective electrodes measure the potential of a solution and the Nernst equation must then be used to determine the concentration of fluoride ions in solution. A buffer must be used to maintain a pH range of 5-9 to provide a uniform background for ionic strength.[7] Ion-selective electrodes are widely applicable because they are easy to use, selective, and provide a wide dynamic range. However, ISE can have long equilibration times, electrode drift, and dissolution of the lanthanum fluoride membrane crystal.[8]

The motivation for the proposed project was the water quality reports in my hometown of Isle of Wight County, Virginia. For many years there has been high levels of fluoride in the drinking water supplied to residents of the county. The latest water quality reports were published from 2016-2019; many were published with an advisory that children should not drink the unfiltered water due to the high concentration of fluoride.[4] This has led many parents, including my own, to pay for Brita water filters and purified bottled water in an effort to protect their children's teeth. In this proposed study, alternative methods for fluoride detection and remediation will be evaluated and a fluoride ion-selective electrode will be used as a base detection method. It has been proven in a number of studies to produce accurate detection readings[7] and will hence be used as a comparison for additional methods.

The ion-selective electrode will be compared to a cyanine dye indicator and an at-home test strip. The use of a silanated cyanine dye as a detection method for fluoride in aqueous solution has been proven effective in a 2005 study. The study concluded that the method had a high sensitivity and specificity. When the silanated dye is mixed with fluoride ions, a chemical reaction occurs in which the fluoride attacks the silicon-oxygen bond, forcing the silicon off of the structure. This chemical reaction can be detected using absorption spectroscopy. The silanated and non-silanated dye absorb at different wavelengths. As the reaction occurs, a peak at 600 nm arises which correlates to the concentration of the non-silanated dye and thus the concentration of fluoride ions in solution[8]

For water supplies that are found to have levels of fluoride that are too high, removal of the excess fluoride is an important step in water treatment. A second part of the proposed project will be the investigation of fluoride remediation techniques. Reverse osmosis is one of the common methods of removal of fluoride and can be used as a standard method to compare with cheaper alternatives such as alumina and Brita filters. Reverse osmosis (RO) is the consequence of high pressure forced upon the side of a solution with a high concentration of fluoride ion that has been separated by a semipermeable membrane. This process removes soluble and particulate matter and has proven to be 90 percent effective at removing fluoride from water.[9]

## Proposed Experiments

### *Sampling*

Samples will be taken from several sources in Isle of Wight County and refrigerated until ready to be analyzed. Sampling will include one filtered and unfiltered source supplied by the county and one from an unfiltered source from a private well. There are 13 different sources of drinking water supplied to residents of Isle of Wight county, each with varying levels of fluoride. Nine of the sources do not receive any treatment.[4]

### *Fluoride Standards*

Fluoride standard solutions will be made using the method of standard addition. The standards will be made at various concentrations to encompass the limit of detection and quantitation of each detection and removal method. They will be prepared by a serial dilution of a sodium fluoride stock solution.[8]

### *Detection: Ion-selective electrode*

Analysis and use of ISE will be based on methods published in Rum et al.[7] Twenty-five milliliters of buffer will be added to the fluoride standards and it will be diluted to 50 mL with deionized (DI) water. The blank will consist of 25 mL of the buffer and 25 mL of DI water. All samples will be diluted 1:1 with the buffer to equal 50 total milliliters. Next, the electrode will be immersed into the solution and the readings will be recorded once stabilized. After each sample reading, the electrode will be rinsed with DI water to prevent any solution carry-over.[7]

*Detection: Cyanine Dyes*

The cyanine dye will be synthesized and purified before being silanated with TBS according to Zhu et al.[8] Water samples will be diluted ten-fold with DI water. A constant volume of an appropriate solvent, the stock cyanine solution, and standard sodium fluoride solution or sample will be mixed and the absorbance at 600 nm will be measured using an appropriate solvent-water (7:3, v/v) solution as the reference.[8]

*Detection: At-home test kit*

Small aliquots of each sample will be placed in a beaker. The test strip will be submerged into the sample for approximately one minute before being removed. The test strip will be compared to the colorimetric reference guide. From the test strip, the presence of fluoride ions will be determined in addition to the pH of the sample.

*Removal: Alumina*

The method will be based on methods used in a study by Tripathy, et al.[10] Activated alumina will be impregnated with aluminum and a pH of $3.5 \pm 0.1$ will be maintained throughout the procedure. The aluminum impregnated activated alumina will be added to a solution with a known concentration of fluoride and shaken vigorously. The solution will be filtered through to remove the alumina and collected in a clean container. The filtered solution will then be analyzed using an ion-selective electrode and the amount of fluoride removed will be determined.[10]

*Removal: Brita Filters*

Standard solutions with known concentrations of fluoride will be placed in a Brita water pitcher and filtered. The filtered solution will be analyzed using an ion-selective electrode and the amount of fluoride removed will be determined.

## Conclusion

From this project, it is expected to develop a technique to inexpensively and easily detect and remove fluoride in drinking water. The results of this project will be shared with the residents of Isle of Wight County in order to inform them of more accessible methods of defluoridation to protect the teeth of their loved ones.

## Timeline

**Late July:** Collection of water samples

**August - Mid October:** Perform all detection method

**Mid October - November:** Perform removal methods

**December - January:** Data analysis and effectiveness rating of methods.

**January - March:** Complete data analysis and write the final paper.

**April:** Poster presentation

## Committee Members

Dr. Andrew Yeagley- Associate Professor, Longwood University

Dr. Melissa Rhoten- Professor, Longwood University

Dr. Julian Bobb- Post-Doctoral Associate, Virginia Commonwealth University

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