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Aluminum Analysis of Water at Columbia College

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ABSTRACT

Water contamination from trace metals can pose severe threats to human and environmental health. The Environmental Protection Agency (EPA) classifies aluminum as a secondary contaminant, for which it provides non-mandatory secondary maximum contaminant levels (SCML) because such contaminants are not considered to present a risk to the public. The SMCL for aluminum is between 0.05 and 0.2 mg/L or part per million (ppm). Tap water from different sources on the Columbia College campus were analyzed for aluminum content by fluorometry and visible spectrometry. The results from the fluorometry method indicated that samples from two locations on campus were higher than the SCML limit for aluminum of 0.2 ppm. The visible spectrometry method was found to be time consuming and ineffective for aluminum analysis due to the necessity of specific reagents and sample preparation.

INTRODUCTION

Water is an essential element of life that contains many different trace metals. Aluminum is one of the most abundant elements in the earth's crust and has a wide range of uses. Aluminum sulfate is added to water to destabilize natural, fine particulate matter in a process called *coagulation* at water treatment plants.[1] However, aluminum sulfate can precipitate under certain pH conditions.[2] Other studies have shown that acidification of lakes and streams by acid rain has transferred aluminum from soil to aquatic environments.[3] Aluminum has been hypothesized to impact human health if the concentration is higher than 0.2 ppm or mg/L, according to the EPA.[4]

Although aluminum is considered a secondary contaminant that only influences taste, color, and odor of drinking water, studies suggest that a higher concentration of aluminum in drinking

water is associated with many health issues. Under a constant exposure to aluminum, animals and humans undergo the risk of developing a range of symptoms, including nausea, skin ulcers, vomiting, and diarrhea.[2] An 8-year study in France showed that aluminum concentration in drinking water of a concentration higher than 0.1 ppm is associated with an elevated risk of dementia and Alzheimer's disease.[5]

Because aluminum is classified as a secondary contaminant, the concentration of aluminum in water is not as highly regulated as other substances and chemicals. The City of Columbia, South Carolina, publishes water quality reports annually to provide consumers with data on water quality. According to the City of Columbia's 2016 Water Quality Report, aluminum concentration was not assessed as a regulated secondary standard.[6] Because some areas in the Columbia were flooded during Hurricane Matthew in October 2016, water quality may have been heavily affected. However, the impact of the flood on aluminum concentration is unknown because this metal is not on the regulated list. Knowledge of the concentration of aluminum in water informs better water treatment methods and more suitable ways to use water sources. Each source of water will differ in aluminum concentration due to differing pipe systems.

This study investigates the concentrations of aluminum at various areas on the Columbia College campus; the recorded concentrations will determine whether or not the water sources on campus have a safe level of aluminum.

Fluorometry is a procedure which measures the intensity of a fluorescent light emitted by a sample in relation to that of a given standard.[7] The samples are treated with a solvent or a mixture of solvents in order to extract the element of interest, which is aluminum in this study. The

intensity of emitted light is measured at an angle of 90˚ to the excitant beam. For quantitative determination, the concentrations of the samples are calculated using the following formula:

$$c_x = \frac{I_x . c_s}{I_s} \qquad (1)$$

where c_x is the concentration of the examined solution, c_s is the concentration of the standard solution, I_x is the intensity of the light emitted by the examined solution, and I_s is the intensity of the light emitted by the standard solution.

In visible light spectrometry, the absorbance of a set of standard solutions with various concentrations of the element of interest is obtained using the visible spectrometer. These absorbance values provide a calibration curve that satisfies Beer's Law and allows for the determination of the element of interest within different samples. The calibration curve follows the basic equation of Beer's Law:

$$A = \varepsilon bc \qquad (2)$$

where A is the absorbance of samples, ε is the molar absorptivity, b is the path length of the instrument, and c is the concentration of each sample. The absorbances and concentrations of standards provide a correlation between these two criteria in the form of a linear line. Using this standard line, the concentrations of samples are determined by plotting their absorbances on the graph.

In this experiment, tap water samples were obtained and tested for aluminum concentration by first fluorometry and then visible spectrometry.

METHODS

Obtaining samples

Tap water samples were obtained from four different locations on campus: Bush Science Center, Breed Leadership Center, Dining Hall, and McNair Residence Hall. Each sample was collected and stored in a 1000 mL Nalgene bottle. All Nalgene bottles were rinsed with deionized water three times before sample collection. Samples were maintained between 20˚C and 23˚C.

Fluorometry method[7]

Solutions Preparation

The fluorometry technique was adapted from European Pharmacopoeia.[7] Acetate buffer solution, pH 6.0, was made by dissolving 33.3337 g of ammonium acetate (Sigma-Aldrich) in 100 mL of deionized water. Then, 1.37 mL of glacial acetic acid (Fisher Scientific) was added to the mixture before the pH of the solution was adjusted with acetic acid or ammonium hydroxide (Fisher Scientific). Finally, the solution was diluted into 167 mL with deionized water.

Samples were prepared for analysis by adding 10 mL of acetate buffer solution, pH 6.0, and 100 mL of deionized water to 400 mL of the testing sample.

The aluminum standard of 2 ppm was prepared from a larger 200-ppm aluminum standard, which was obtained by dissolving 0.352 g of aluminum potassium sulfate dodecahydrate (Sigma-Aldrich) in 10 mL of dilute sulfuric acid (5.5 mL of sulfuric acid in 94.5 mL of deionized water) and diluting to 100 mL with deionized water. One mL of the 200 ppm solution was then diluted to 100 mL to obtain the 2 ppm aluminum standard.

The standard solution was a mixture of 2 mL of the aluminum standard solution, which contained 2 ppm of aluminum, 10 mL of acetate buffer solution, pH 6.0, and 98 mL of deionized waster.

The blank solution was made from mixing 10 mL of acetate buffer solution, pH 6.0, and 100 mL of deionized water.

Fluorometer Setup

The sample solutions, each 510 mL, were placed in a separatory funnel and shaken with two quantities, each 20 mL, and then with one 10 mL quantity of a 5 g/L solution of hydroxyquinoline (Sigma-Aldrich) in chloroform (Fisher Scientific). The combined chloroform solutions were diluted to 50 mL with chloroform. The standard and blank solutions were prepared in the same manner. All standards and samples were analyzed in an Agilent Cary Eclipse Fluorescence Spectrometer with a start beam of 412 nm, stop beam of 650 nm, and a band slip of 5 nm. The intensity of the fluorescence of the samples, standard, and blank, were measured at the excitant beam of 392 nm and the transmission beam centered at 518.05 nm.

Samples were allowed to sit for 1 week before analysis in Trial 2 and for 2 weeks before analysis in Trial 3.

Visible spectrometry method[8]

Solution Preparation

The stock aluminum solution was prepared by dissolving 0.879 g of aluminum potassium sulfate dodecahydrate (Sigma-Aldrich) in 100 mL of deionized water. Then, 10 mL of this solution was diluted to 1000 mL with deionized water.

To make the ascorbic acid solution, 0.1 g of L-ascorbic acid (Fisher Scientific) was dissolved in 100 mL with deionized water.

The buffer reagent was made by dissolving 136 g of sodium acetate (Flinn Scientific, Inc.) in water and then adding 40 mL of 1 M acetic acid. The resulting solution was diluted to 1000 mL with deionized water.

Stock dye solution was obtained by adding 150 mg of eriochrome cyanine R (Sigma-Aldrich) to 50 mL of deionized water. The pH of this solution adjusted to about 2.9 with 50% acetic acid in water. Finally, this solution was diluted to 100 mL with deionized water. The working dye solution was prepared by diluting 10 mL of the stock dye solution to 100 mL with deionized water.

Methyl orange indicator solution was made by diluting 0.0501 g of methyl orange powder (Eastman Organic Chemicals) in deionized water. The ethylenediaminetetraacetic acid (EDTA) solution was prepared by dissolving 0.3708 g of sodium salt ethylenediaminetetraacetic acid dihydrate (Fisher Scientific) in water and then diluting to 100 mL with deionized water.

Standards solutions for the Beer's Law graph were prepared by diluting 0 mL to 0.7 mL portions of the aluminum working standard to approximately 25 mL in 50 mL volumetric flasks. One mL of 0.01 M sulfuric acid, 1 mL of ascorbic acid solution, and 10 mL of buffer reagent were added to each flask. With a volumetric pipette, 5 mL of working dye solution was added, and the flasks were diluted to the mark with deionized water. The solutions were allowed to stand for 10 minutes before analysis.

A few drops of methyl orange were added to 25 milliliters of sample which was then titrated with 0.01 M sulfuric acid to a faint pink color. The amount of acid used was recorded. Then, two new 25 mL portions of sample were added to 50 mL volumetric flasks. To each of these samples was added the volume of 0.01 M sulfuric acid required for the titration plus 1 mL excess. One

mL EDTA solution, which would serve as a blank, was added to the sample. One mL of ascorbic acid solution, 10 mL of buffer reagent, and 5 mL of working dye solution were added to both samples, and the resulting solutions diluted to 50 mL with deionized water. The samples were allowed to stand for 10 minutes before analysis in Trial 1. Samples were allowed to sit for 1 week before analysis in Trial 2 and for 2 weeks before analysis in Trial 3.

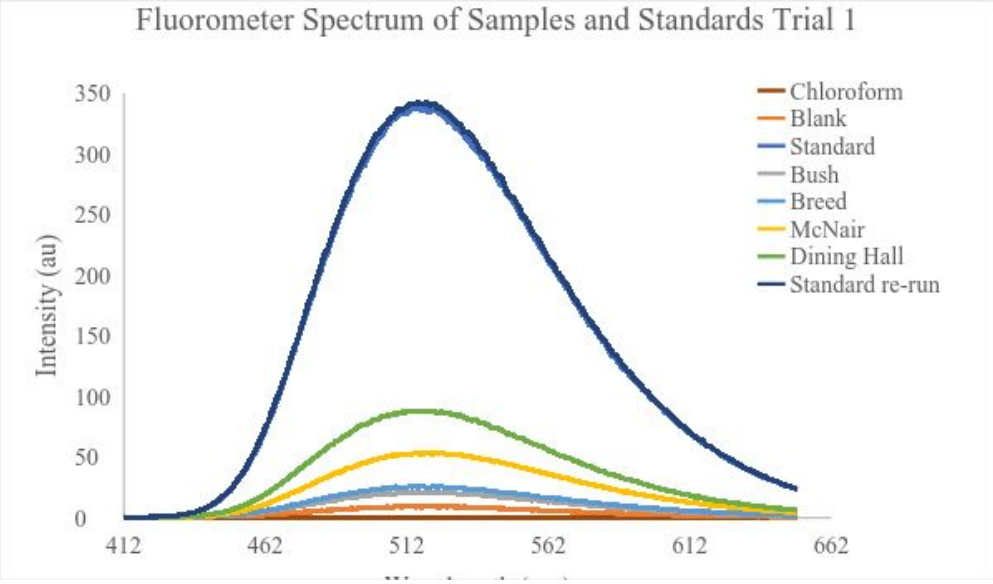
Visible Spectrometer Setup

The standards and samples were placed into the spectrometer (Thermo Scientific, SPECTRONIC™ 200) to obtain absorbance. The target wavelength for this experiment was between 525 nm and 535 nm.

RESULTS

Fluorometry method

All samples were analyzed in triplicate to obtain the mean aluminum concentration. The 2 ppm aluminum standard was run before and after the sample analysis to mitigate deviation based on the percent recovery of standard. Chloroform as a diluent was also analyzed to ensure there was no aluminum present.



Trial 1 of the experiment was analyzed immediately after sample preparation. This represents the original results of samples and standards and is considered the initial data for the experiment. Sample stability was tested in Trial 2 a week after sample preparation, and that of Trial 3 was tested 2 weeks after sample preparation. All samples and standards were stored in a refrigerator at 8˚C and sealed with parafilm.

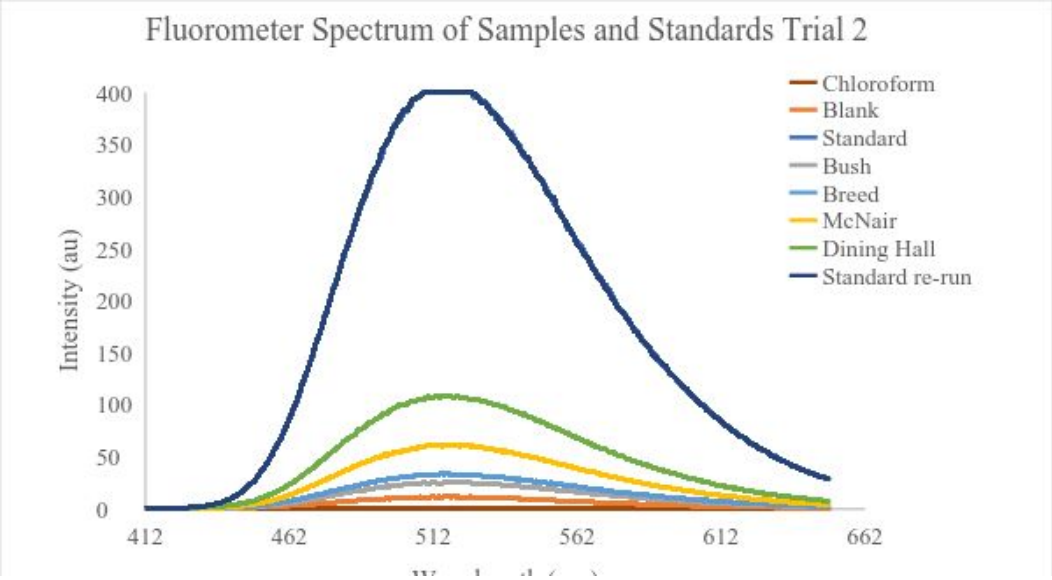
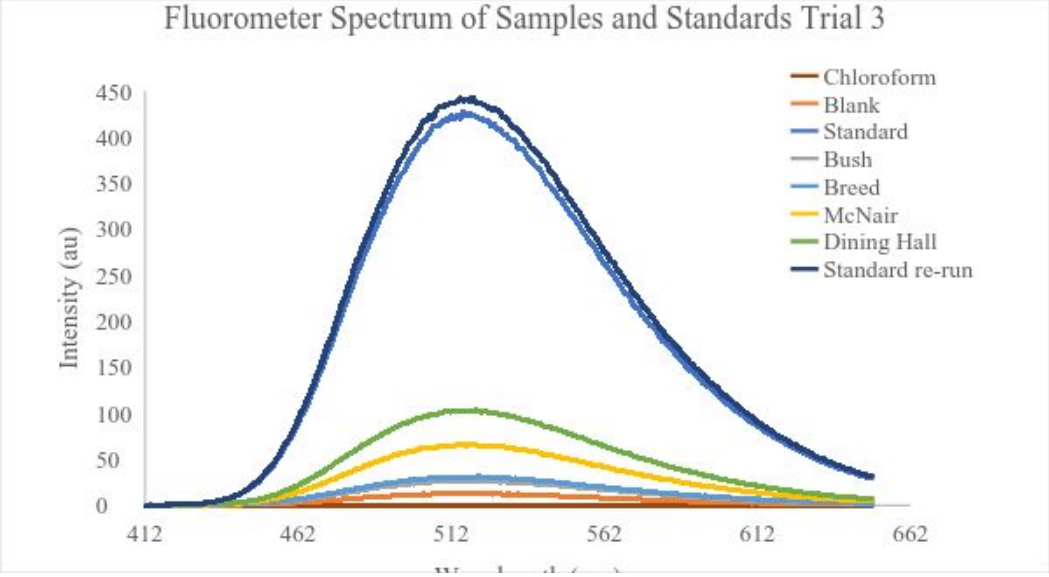


Fig SEQ Figure * ARABIC 2 Spectra obtained from rial 2 of the luorometry method (week after sample preparation)



The spectra of the three trials show similar trends for chloroform, standard, and samples. A summary of results is presented in Table 1, without a baseline correction for the blank in order to reflect the original results for each trial. All results are recorded to four decimal places.

Sample	Trial 1	Trial 2	Trial 3	Average
Blank	0.0550	0.0566	0.0600	0.0572
Bush	0.1231	0.1231	0.1271	0.1244
Breed	0.1526	0.1622	0.1440	0.1529
McNair	0.3147	0.2983	0.3104	0.3078
Dining Hall	0.5202	0.5276	0.4824	0.5101

Fig SEQ Figure * ARABIC 3 Spectra obtained from rial 3 of the luorometry method (weeks after sample preparation)

Table 1 Aluminum concentration from each sample without baseline correction with respect to blank and chloroform. This represents the raw data after using Equation (1) to obtain aluminum concentration.

The following tables present data for the initial intensity of chloroform, standard, blank, and samples. Baseline correction is applied by subtracting the intensity of chloroform and then the blank from the initial intensity of all samples, illustrating the final representative aluminum concentrations of samples. These results are used to determine if samples pass or fail the SMCL of 0.2 ppm set by EPA.

Sample	Initial Intensity	Intensity (without Chloroform)	Intensity (without Blank)	Final Concentration (ppm)
Chloroform	0.2108	0.0000	N/A	N/A

Blank	9.2584	9.0476	0.0000	0.0000
Bush	20.7213	20.5106	11.4630	0.0700
Breed	25.6881	25.4773	16.4297	0.1004
McNair	52.9678	52.7571	43.7095	0.2670
Dining Hall	87.5619	87.3511	78.3035	0.4784
Standard	336.6403	336.4296	327.3819	2.0000
Standard re-run	341.5701	341.3594	332.3117	2.0301

Table 2 Final aluminum concentration of samples in Trial 1 after baseline correction from which chloroform and blank intensity was subtracted from original intensity values. Using Equation (1), final concentration of aluminum is obtained. Samples from McNair and Dining Hall are higher than the SMCL from EPA.

Sample	Initial Intensity	Intensity (without Chloroform)	Intensity (without Blank)	Final Concentration (ppm)
Chloroform	0.1438	0.0000	N/A	N/A
Blank	11.6047	11.4609	0.0000	0.0000
Bush	25.2221	25.0783	13.6174	0.0684
Breed	33.2266	33.0828	21.6219	0.1086
McNair	61.1033	60.9594	49.4986	0.2487
Dining Hall	108.0853	107.9415	96.4806	0.4847
Standard	409.6906	409.5468	398.0859	2.0000
Standard re-run	409.4398	409.2960	397.8351	1.9987

Table 3 Final aluminum concentration of samples in Trial 2 after baseline correction. Samples from McNair and Dining Hall are higher than the SMCL from EPA.

Sample	Initial Intensity	Intensity (without Chloroform)	Intensity (without Blank)	Final Concentration (ppm)
Chloroform	0.1804	0.0000	N/A	N/A
Blank	12.7476	12.5671	0.0000	0.0000
Bush	26.9995	26.8190	14.2519	0.0692
Breed	30.5941	30.4137	17.8465	0.0866
McNair	65.9254	65.7449	53.1778	0.2581
Dining Hall	102.4639	102.2835	89.7163	0.4355
Standard	424.7747	424.5943	412.0271	2.0000
Standard re-run	439.2925	439.1121	426.5449	2.0705

Table 4 Final aluminum concentration of samples in Trial 3 after baseline correction. Samples from McNair and Dining Hall are higher than the SMCL from EPA.

Final aluminum concentrations are illustrated in Table 5 with obtained average results and standard deviation for each sample after baseline correction. Based on the average results, samples that were higher than the SMCL could be identified.

Sample	Trial 1	Trial 2	Trial 3	Average
Blank	0.0000	0.0000	0.0000	0.0000
Bush	0.0700	0.0684	0.0692	0.0692 ± 0.0008
Breed	0.1004	0.1086	0.0866	0.0985 ± 0.0111
McNair	0.2670	0.2487	0.2581	0.2579 ± 0.0092
Dining Hall	0.4784	0.4847	0.4355	0.4662 ± 0.0268

Table 5 Summary of aluminum concentrations of samples after baseline correction. Samples from McNair and Dining Hall, displayed in red, fail the aluminum test with concentrations higher than 0.2 ppm.

Visible spectrometry method

There was no data obtained from the visible spectrometry method due to errors in method interpretation or execution. The standards were made following the method and color was visualized within 15 to 20 minutes. However, the method employed did not result in samples or standards that were stable enough for visible light detection. After preparation, the solutions rapidly lost color.

DISCUSSION

Heading about the fluorometry method

Figure 1 showed no emission signal of chloroform at a transmission peak of 518.05 nm. The blank exhibited maximum peak at 518.05 nm, which indicated that a certain concentration of aluminum was present. The recovery of the standard was relatively efficient, demonstrating the precision of the measurements and the insignificance of the chloroform evaporating. The same phenomenon was observed in Figure 2. However, the standard showed higher efficiency in recovery before and after measurement than in Trial 1. Figure 3 demonstrated the least efficient

recovery rate of standards. However, chloroform still did not show any emission peak at 518.05 nm while the blank still presented a signal.

Based on information obtained from the fluorometry method in Table 5, the water sample from the Dining Hall had the highest aluminum concentration (0.4662 ± 0.0268 ppm) of the four samples collected from the Columbia College campus. The second highest was that of the McNair Residence Hall (0.2579 ± 0.0092 ppm). These were the only locations that had aluminum concentrations higher than the EPA's secondary maximum contaminant level of 0.2 ppm. The old piping systems of the Dining Hall and the McNair Residence Hall are reasonable explanations for the high aluminum concentration of the buildings' water sources.

The data was consistent among the three trials (see Figures 1, 2, and 3). The amount of time between sample preparation and analysis did not impact the data significantly. It was hypothesized that the volatility of chloroform as a diluent would impact the intensity of signals over time. Consequently, results from Trial 2 were expected to be higher than those of Trial 1 and lower than those of Trial 3. All the results obtained from Trial 1 were lower than those from Trial 2 (see Tables 2 and 3). However, all standard and sample solutions were stored under the same conditions, which eliminated the effects of chloroform evaporation. Comparison of Tables 3 and 4 prove that intensities of samples from the Breed Leadership Center and Dining Hall are lower in the case of samples tested 2 weeks after sample preparation than samples tested after 1 week. A noticeable point from the obtained results is that the chloroform and blank samples had aluminum content because they had fluorometry signals. The signal in chloroform indicated that there could be some aluminum content in the chloroform from the glass chloroform container. In the case of the blank, sample preparation using glassware that was not acid washed could have

introduced aluminum contamination. Additionally, the deionized water was not tested for a fluorometer signal. The old water purification system could be a potential aluminum source in the blank.

Heading about the visible spectrometry method

With the visible spectrometry method, no results were obtained for samples collected at Columbia College. Standards were prepared following the method outlined, but color stability was not maintained throughout the course of the experiment. According to the method referenced[8], all standards were allowed to stand for 10 minutes after being diluted to the correct volume. The analysis with the visible spectrometer was performed right after the 10-minute standing period, but the color faded before the analysis could be completed. This problem was encountered in the sample preparation.

Another possible error with the visible spectrometry method involved the pH adjustment of stock dye solution. The method stated that the beginning pH of stock dye solution should be around 9.0 and adjusted to a 2.9 pH. In preparation for the stock dye solution, the initial pH of this solution was below 2.9 pH units when prepared with 150 mg of eriochrome cyanine R (Sigma-Aldrich). Therefore, the amount of eriochrome cyanine R was lowered to about 75 mg to obtain an initial pH greater than 2.9 pH units. This variation could affect color development and the stability of samples. An evaluation was performed on the preparation of stock dye solution. It was determined that there were two listed vendors for eriochrome cyanine R with different amounts of reagent used. Therefore, to address this issue, eriochrome cyanine R must be purchased from the two vendors listed in Bartram and Balance's procedure.[8]

CONCLUSION

By using the fluorometry method, concentrations of aluminum in tap water were successfully measured. A second analysis using visible spectrometry was attempted unsuccessfully. With the fluorometry method, it was determined that the Dining Hall and McNair Residence Hall had higher concentrations of aluminum than the secondary maximum contaminant level set by the EPA. No data was generated from the visible spectrometry method because of errors in method interpretation or execution.

This study serves as foundation for water research for undergraduate students and monitoring water quality on the Columbia College campus. Other research topics related to diagnosing water quality that can be explored include determining the hardness of water (calcium and magnesium) and the concentrations of zinc, mercury, and organic matter. As for analyzing the concentration of aluminum in water, future exploration includes successfully conducting the visible spectrometry analysis for the samples to compare with the results obtained from the fluorometry method. Furthermore, new methods to analyze aluminum concentration in water could also be employed and examined.

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