Anastasija Cumika

Water Filtration NMR spectroscopy

PHT-431-01

14 April 2019

Abstract

This experiment was performed to find out the purity of the water after the filtration with the Great Value Filter Pitcher with the NMR spectroscopy technique. We measured T_1 for each water sample, and the longer T_1 time the more pure water sample is. We compared the results with initial sample of tap water, samples from the Dolphin Den fountain drink machine and Science Center filter bottle refill, as well as a sample of water from the Den with salt added to it (salted water). We found out that tap water is the least pure with T_1 time 2.38 ± 0.12 s. In addition, we proved that it is enough to filter the water once through the filter and our approximate result for T_1 of the filtered samples is 2.56 ± 0.05 s. We concluded that Great Value Filter is not a good quality, because the T_1 of the filtered samples is shorter than T_1 of the Science Center sample or the Den sample, as well as the salt-water sample T_1 value falls within the range of that filtered water sample T_1 value.

Introduction

Water is one of the most important sources for human, and drinking clean water protects the body from disease and leads to overall greater health and energy. Unfortunately, the tap water has a lot of metals, salts and chemicals in it, such as chlorine, pesticides, cooper and lead. For example, exposure of lead in the water can affect the nervous system, muscle growth and bone health. While chlorine is the cause of unpleasant taste of the water. Therefore, people are using the filters to clean the water we use for cooking and drinking. In addition, water filters reduce risk of certain cancers and gastronomical diseases [1].

Usually, we filter the water only once, considering that after one filtration water is clean. The question arises: is it enough to pass the water through the filter once to clean the water off impurities. To answer this question, we decided to use the Nuclear Magnetic Resonance (NMR) spectroscopy to study the purity of the water samples that were filtered through the water filter different amount of times along with some control samples.

NMR was discovered in 1946, when two groups simultaneously discovered the fact that a sample, that has a magnetic nuclei, placed in the uniform magnetic field responds to the continuous radio frequency (CW) magnetic field when the frequency of the field is tuned to the radio frequency [2]. Since that discovery NMR became a very important techniques used by physicists, chemists and other scientists.

Magnetic nuclei is a nuclei that has angular momentum and magnetic moment, in other words they have a property called spin. The nuclei that has their angular momentum collinear with magnetic moment, such as protons (hydrogen nuclei) and fluorine nuclei are easy to study with NMR [3]. Such a property gives an opportunity to observe that when the external uniform field is applied, magnetization vectors of all the nuclei align with the external magnetic field and we can observe net magnetization M. Water contains a lot of hydrogen (protons), therefore NMR is a great choice to study the water samples.

The condition when net magnetization is maximum is called a thermal-equilibrium condition. The time that it takes for the sample to reach its magnetization thermal-equilibrium (go from initial net magnetization to max net magnetization) is almost always exponential and is characterized by the spin-lattice relaxation time constant T_1. Magnetization as a function of time is described by the differential equation shown in Equation 1, where M_0 is the equilibrium magnetization (max magnetization) and M_z is the instantaneous magnetization [3]. The solution to this equation depends on the initial magnetization and results in exponential relationship between magnetization and time.

$$\frac{dM_z(t)}{dt} = \frac{M_0 - M_z(t)}{T_1}$$

[1]

Since usually the time it takes for the sample to reach its thermal equilibrium is very small, for this experiment, we choose to have our initial magnetization to be $-M_0$. Such a choice for initial condition increases the time of remagnatization, so we can get a better data as well as better uncertainty. Using this initial condition, we solve the Eqution1 and the solution is shown in Equation 2. From the solution to the Equation 1, we observe that, we can extract the value for T_1 by measuring the magnetization as a function of time.

$$M_z(t) = M_0 - 2\, e^{-\frac{t}{T_1}}\, M_0 \qquad [2]$$

However, magnetization measurement gets tricky because of the way the instrument is build. To measure the magnetization we are using the sample coil. Magnetization induces the current in the coil that apparatus measures and we can observe the Free Induction Decays (FID) signal on the oscilloscope. The diagram on the Figure 1 shows that the magnetization has to be in the y direction so that we can measure it. However, the magnetic field is in the z direction which makes the net magnetization is in the z direction. To make it possible to measure the magnetization we want to rotate the magnetization onto the x-y plane.
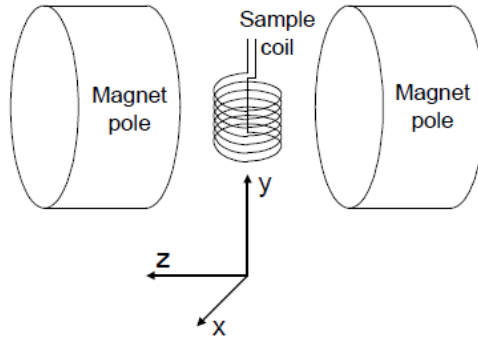

Figure 1: Schematic of permanent magnet and sample coil orientation within the coordinate system [1].

The sample coil has another role, the transmitter, which supplies oscillating RF field that can change the orientation of the magnetization. Once magnetization is rotated some angle away from the z-axis it rotates around the z-axis because angular momentum vector stayed in the z-axis direction.

To measure actual magnetization that is in the z direction we want to rotate our pulse to 90° so that our magnetization is in the x-y plane. Such as pulse is called a 90° pulse. The duration of the pulse determines to what degree we rotate the magnetization. If we apply the pulse for the time twice longer then what it takes to have 90° pulse we will again observe no magnetization because it was rotated 180°. Important to know that the coil can only do one role at the time, so we cannot measure the magnetization during the RF pulse [3].

3

To measure the magnetization after some time t we perform two pulse sequence. First we apply 180° pulse that rotates magnetization to the $-M_z$ initial condition as described above. The second pulse we apply after some time t (delay time), which rotates the magnetization to x-y plane where we can measure it. The maximum FID amplitude is directly proportional to the magnitude of M_z at the time when the second pulse occurs [2].

The characteristic times T_1 depend on the purity of the material. During the magnetization, the energy flows from nuclei to the surrounding, where surroundings are "the lattice", which are all other spin states of protons and not protons that are around the nuclei. When one nuclei magnetizes it releases the energy in terms of angular momentum to the surroundings, which acts like a sink to all the extra momentum. In the perfectly pure water, all the protons are the same and when one changes the state from down to up, the released energy is just enough to change the neighboring nuclei state from up to down. However, when we have impurities, some nuclei might need, for example, five times more energy to change the state than other nuclei. Since the energy is not equally spread out, it takes less time to magnetize the sample, which is less pure. As the amount of impurities in water decreases, T_1 characterization time increases. In the case of the water sample, the higher concentration of impurities results in the more surroundings for each nuclei. Therefore, cleaner water has longer T_1 time.

Procedure

The instrument

For this experiment, we are using the TeachSpin PS2-A NMR spectrometer. This instrument was designed specifically for education purposes and can be used to study two types of nuclei, protons (hydrogen nuclei) and fluorine [3]. The instrument consists out of four modules, but we are using only three. Synthesizer and Pulse Programmer are used to control the RF pulse signal. Receiver module is in charge of the sample coil, so it does two functions – sending the RF pulse to the coil and receive the induced current information form the coil. The signal received we observe on the oscilloscope by connecting receiver Env.Out output to the oscilloscope Ch1. From the receiver module we also get the mixer signal that is going form the output Q or I (for this lab I used output Q). The Pulse Programmer Module also has a Sync output that we use for trigger pulse to trigger our signal on oscilloscope and FFT Analyzer. For this instrument, there were multiple connections in between modules. Those connections are described in the instructor manual in the chapter "The Instrument" [3].

PS2 NMR spectrometer comes with the permanent magnet and the control panel that controls the magnet. The magnet is made out of NdFeB and its magnetization is temperature dependent. The temperature control is built in the magnet, where the temperature is maintained with the thermoelectric cooler modules. The

temperature control knobs, one for each side of magnet, are located on the left of the magnet control panel as shown on Figure 2. Since the magnet is temperature sensitive do not place the magnet in a draft, near ventilator or a radiator heater. Also, since magnet is strong do not have any significant ferromagnetic materials nearby and do not place a magnet nearby AC high power lines [3].

Figure 2: Magnet control panel [2].

Preparing the Samples

For this experiment, we are using the Great Value Water Filter Pitcher (model# QP5-01) manufactured by Brita LP. Manufacturer claims that filter has three actions: "Ion exchange resin reduces harmful substances", coconut activated carbon reduces metals and the micro-mesh filtration removes any remaining particles. Before starting the water filtration, follow the instruction on the filter box for preparing the filter cartridge.

Each sample of water we put in the small beaker that is a little taller than 40 mm. It is important to use the correct volume for the experiment, which is about 5 mm from the bottom of the beaker as shown in Figure 3 [3]. On each beaker, we put a cap and an O-ring that is placed 39 mm from the middle of the sample. When filling up the beakers make sure to have no water drops stick to the sides of the beaker. We used a paper towel to absorb water from the sides of the beaker. In addition, after the beaker samples were filled up, we let them sit in the upward position for the night before the experiment, so all the water is settled at the bottom of the beaker. Finally, if you are using any dishes during the experiment for the water, make sure to wash it before using.

We got the tap water and our first sample we labeled it as #0 because it is an unfiltered water. Then we pass the water through the filter and use part of that filtered water as our sample #1. We filtered the remaining water again and prepared sample #2. In the similar way, we prepared nine samples where the last sample is labeled #8 and it was filtered eight times.
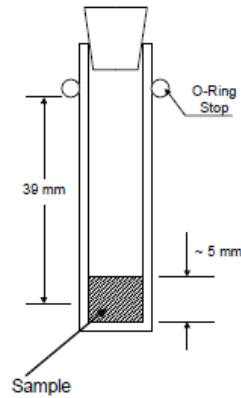
Figure 3: The schematic of the sample

In addition, for the reference we got couple more samples from different sources. We took water samples from the science center water filter (the one that is used to fill up the water bottles) and from the Dolphin Den fountain drink machine. Finally, we added a little bit of salt to the water from the Den and created a third reference sample. The salted water even had a little salty taste to it.

Tuning the apparatus

Before making any measurements we have to perform the tuning of the instrument to set it ready for the experiment. Before turning on the equipment make sure that all the dials on the magnet control panel are set to zero and temperature feedback loops are open. After we turn the instrument on, we have to set the temperature on the magnet. To do so, start dialing the temperature knobs until the error signal indicators start going from red color to dark shade of red (almost brown) and set the loop to closed.
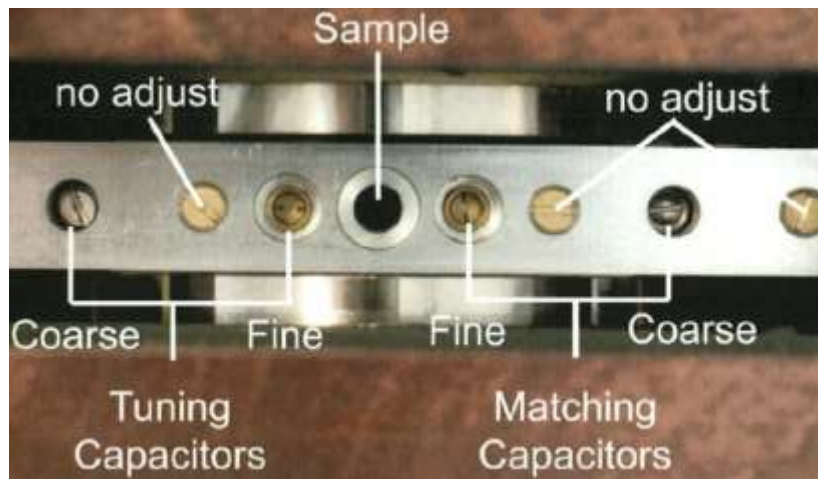

Figure 4: Top view of the permanent magnet. Front side of magnet is on the bottom of the picture [3].

Important note: after all the experiments are finished, one has to make sure to open the temperature feedback loop on the magnet control panel. Then we used the RF probe to tune the tuning capacitor so that sample coil is in resonance with the applied RF signal. On Figure 4, one can observe which knob corresponds to which capacitor as from the top view of the magnet.

On the RF probe there is an O-ring that determines how deep does RF probe go into the sample coil. Set O-ring to 39mm from the middle of the coil. Set the RF probe into the sample coil and connect it to the oscilloscope. Set A-Len on the Pulse Programmer to 2.5 µs and period to 100 ms. One should observe the FID signal as shown in Figure 5. The signal is in the microsecond range, so we had to set oscilloscope time base accordingly to find the FID signal. The goal is to tune the coarse tuning capacitor so it maximizes the FID signal observed on the scope.
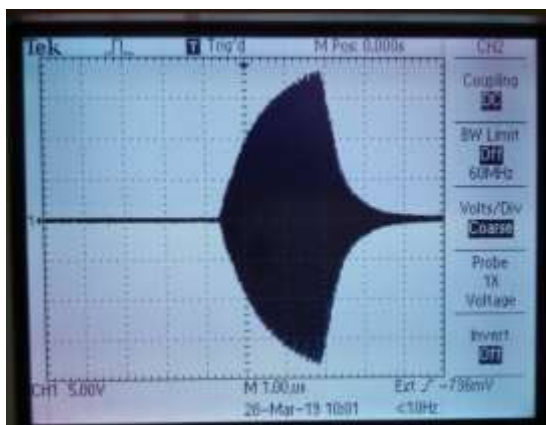

Figure 5: tuned FID signal of the reference probe.

Once RF signal and sample coils are in resonance we have to put them in resonance with the Lamar frequency of the sample. Connect synchronizer Env.Out output to the oscilloscope Ch1, Q output to Ch2 and Pulse Programmer sync output to trigger. Set oscilloscope to trigger on external, probe attenuation 1X and time base to milliseconds range.

On the instrument, we set A-Len to 1.6 µs (can be anything between 1 µs and 2 µs) and frequency to 21.4 MHz, which is our close guess for the proton frequency. Set the O-ring on the mineral oil 39 mm above the center of the sample. It is convenient to use mineral oil sample for tuning because it has small T_1 times, therefore we can sat a relatively small period, around 300ms. Insert the sample probe into the magnet sample coil and observe the FID and mixer signals on the oscilloscope. In the beginning, we see many beats on the mixer signal (as shown on the left of Figure 6), which means that RF signal is not in the resonance with the sample Lamar frequency. Adjust the synchronizer frequency to get rid of the beats and make mixer signal as long as possible. In addition, adjust the reference phase to make mixer signal look like the FID signal.

7

Our next step is to homogenize the magnetic field as much as possible by adjusting the magnetic gradient coils. We want to make our FID signal as long as possible, which shows that our field is relatively homogeneous. Adjust the field gradients X-Y-Z-Z^2 in sequence and then adjust the frequency to eliminate the beats. Repeat the iteration multiple times until the longest possible FID signal is reached. Adjust Ref.Phase again to make mixer signal alike. On the right of Figure 6, one can observe how my signal looked after the frequency, phase and gradient tuning.
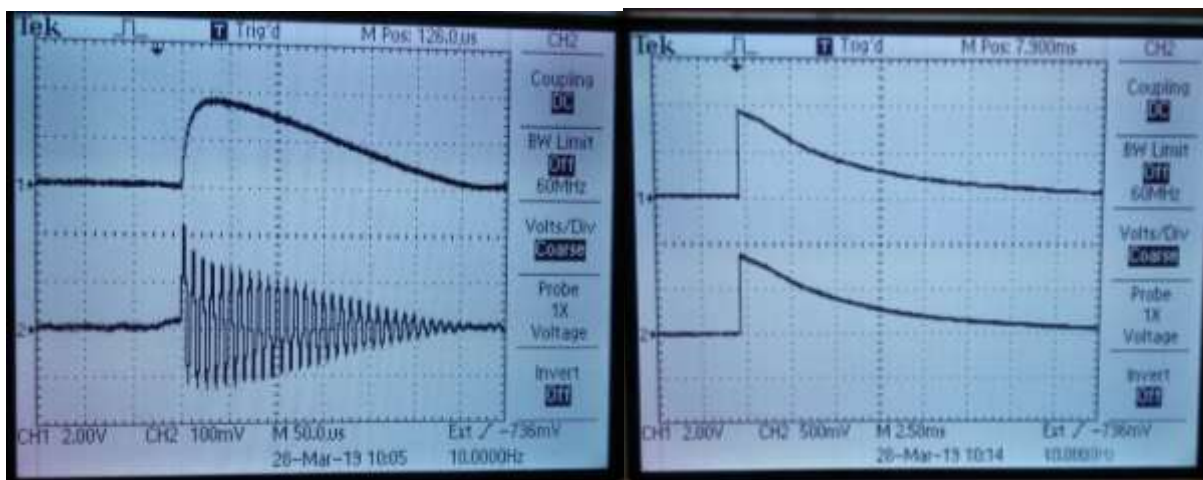

Figure 6: On the left – signal before the frequency, phase and gradient tuning. On the right – signal after the tuning.

The last step in the tuning process is to eliminate the "ringdown" signal that comes from the differences in the synchronized RF pulse and natural sample coil resonant frequencies. Make A-Len pulse 0.2 µs and start increasing it. One should observe the FID signal height increase simultaneously with A-Len pulse increase. At some point FID signal reaches max and starts decreasing. Set A-Len to the value that maximizes the FID signal. This A-Len is our estimate of 90° pulse. Double the pulse to make it a 180° pulse. One should observe the signal to be almost flat. The reason it is not flat is because of the "ringdown". Turn the fine tuning capacitor to minimize the FID. As minimum is reached, turn fine tuning capacitor 1/8 or a full rotation and adjust the A-Len pulse to make FID signal completely flat. If the signal does not go flat, try turning the fine tuning capacitor 1/8 rotation on the other direction (that would be twice 1/8 rotation opposite direction from what turned before) and adjust A-Len. Once flat FID achieved, A-Len is our 180° pulse and half of that A-Len value is our 90° pulse. Record these pulse length values. Set A-Len to 90° pulse and one last time, adjust frequency and ref.phase and record these values.

T_1 characterization time measurement

Water samples are more pure that mineral oil samples, therefore we expect a much higher T_1. This means that we have to increase out repetition period time. We want to aim for period to be ten times greater than

T_1. We found a relative T_1 time by approximately finding the time when magnetization crosses the zero value, similar procedure described below. The good period for the measurements with the water samples we have is 26 seconds.

Set A-len pulse to the value of 180° pulse and B-len pulse to the value of 90° pulse. The B-len pulse repetition N is 1, because we want to rotate the pulse only once. We observe the FID signal on the oscilloscope and we measure the maximum FID amplitude for different delay times applied. On the oscilloscope, it is very convenient to use the cursor to measure the peak of the signal. In addition, make sure to record the uncertainty for the FID amplitude measurement. The delayed times are controlled by τ on the pulse programmer. As we increase τ, our max FID amplitude decreases and at some point crosses zero and start to increase again, which is our magnetization zero crossing point. Even though oscilloscope shows all the amplitudes as positive, all the amplitudes before the zero crossing mark should be recorded as negative because we started at $-M_z$. In addition, measurements around the zero have high uncertainty so it is fine to have a bigger step around M_z equals zero. In total we aim for around 15-20 points in the good range before and after the zero crossing point. When enough data is collected, we plot the FID max amplitude versus the time τ and extract the T_1 characteristic time from the exponential fit on the data points. Repeat the procedure and find T_1 characteristic times for all the samples.

Results

In total, we collected data for twelve samples: tap water, filtered water from one to 8 times, water from the Dolphin Den fountain drink machine, water from Den with salt and water from Science Center water battle filter. We created a plot, such as shown in Figure 7, for each sample.
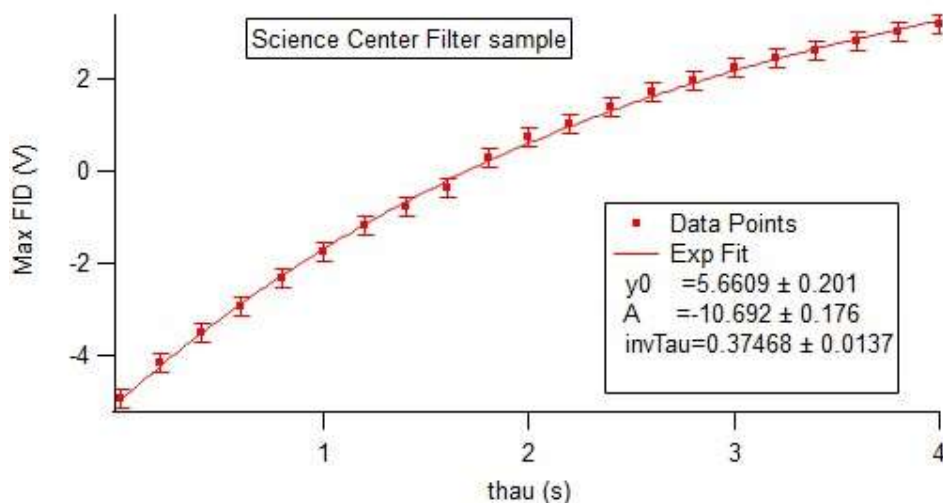

Figure 7: An example of the plot for extracting T_1 from the collected data set for each sample

On each data set, we did an exponential fit and the parameters for the fit are shown in the legend on the plot. All parameters come with the corresponding uncertainty. T_1 is the characteristic time constant for the exponential function that we are fitting and we can find it by calculating the inverse of the invTau parameter. We calculated T_1 for each sample and the results are summarized in the plot on Figure 8. The #0 sample is the unfiltered tap water. The following samples from #1 to #8 are the filtered samples where number of the sample corresponds to the amount of times this water sample was filtered. The last three samples are the control samples: #1 is the sample from the Den with salt, #12 is the sample form the Science Center bottle filter and #13 is the sample from the Den fountain drink machine. The uncertainty on each data point comes from the uncertainty of the invTau parameter for each sample.
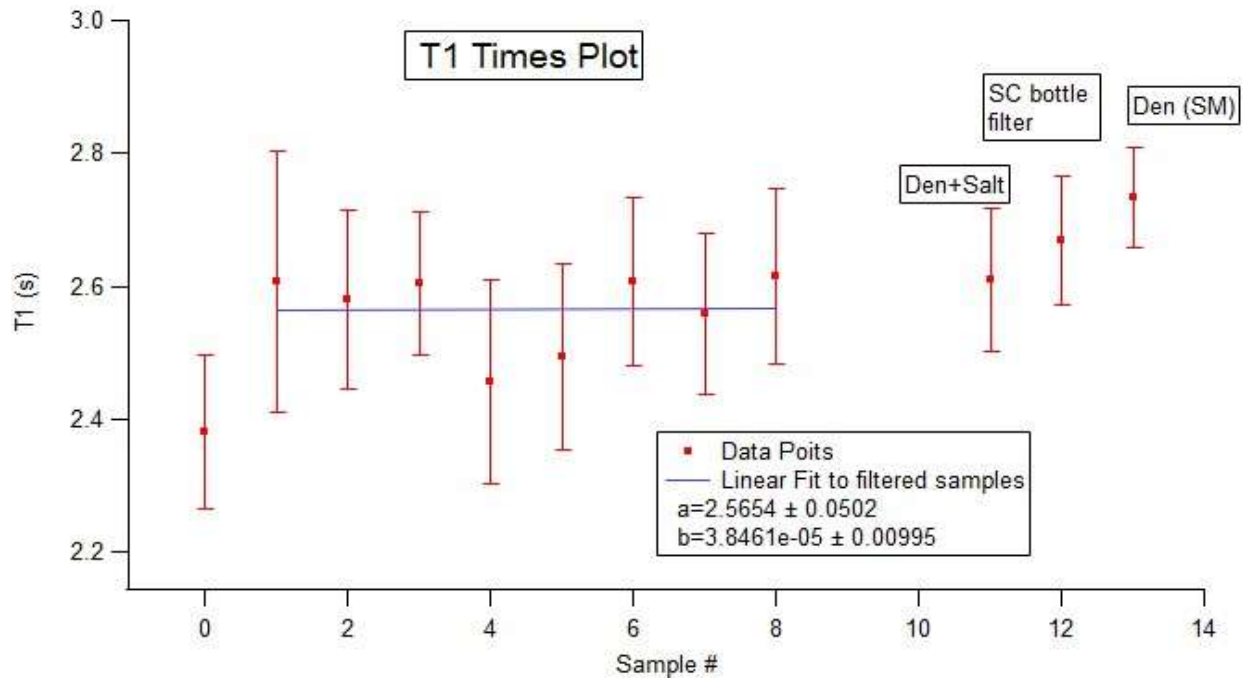

Figure 8: Summarized T_1 times for all the samples on one plot

On the plot, we can clearly see that the tap water sample has the shortest T_1 time – 2.38±0.12 s, therefore this sample has the largest amount of impurities in the sample, which is that we expected. Looking at the data set for the samples #1 through #8 we can state that it is enough to filter the water only one time, because after the first filtration the T_1 of the water sample does not get longer. The values for the T_1 for each filtered sample in order are the following: 2.6±0.2 s, 2.58±0.13 s, 2.61±0.11 s, 2.46±0.15 s, 2.50±0.14 s, 2.61±0.13 s, 2.56±0.12 s, 2.62±0.13. We performed the linear fit on these eight data points, which is the blue line across the points, and the parameters of the fit are represented in the legend on the plot. Our slope is very small – 3.846±0.010, which means that the values together are close relatively to each other, which proves that there is no improvement after the first filtration. Keeping in mind that our slope is minimal, we take

10

the y-axis crossing point as our value for the filtered water sample and it is 2.56 ± 0.05 s. The uncertainty value gives us the range of T_1 for filtered water: $2.51 - 2.61$ s. Interesting point is that this value has a smaller uncertainty than any of the samples uncertainties. We use this value to compare it to the control samples.

The salt-water sample T_1 time, which is 2.61 ± 0.11 s, falls within the range of the filtered water T_1 times. This means that filter did not clear all the particles from the sample and there are still some impurities in the water. With the fact that salted water had enough salt that it even had a salty taste to it, we state that the filter is not a good quality. The Science Center filter water sample has T_1 of 2.67 ± 0.10, is out of the range of the filtered water samples, therefore we can state that the water from the Science Center filter for water battle refill has cleaner water than water from the Great Value Filter. The water from the Dolphin Den fountain drink machine appeared to be the cleanest water from all of the samples and it has T_1 of 2.73 ± 0.07s.

Conclusion

The results from our experiment showed that tap water is indeed the least pure water out of all the samples tested with T_1 time 2.38 ± 0.12 s. We also found out that water purity does not get better after one filtration, so from the linear fit on all eight filtered samples (one time filtered through eight time filtered) and found that T_1 for the filtered sample is 2.56 ± 0.05 s. Comparing this value with the control samples we found out that the water from the Great Value Filter Pitcher is not as pure as the water from the Science Center for bottle refill ($T_1 = 2.67\pm0.10$ s) or from The Dolphin Den fountain drink machine (T_1 of 2.73 ± 0.07s). While the salt water has T_1 (2.61 ± 0.11 s) is within the uncertainty of the filtered sample. Summarizing all the observations of our results, we state that it is enough to filer the water through the filter once. However, the Great Value Filter Pitcher is not a good quality filter. Finally, the purest water out of our samples is the water from the Dolphin Den fountain drink machine.

References

[1] "Ten Reasons To Filter Your Tap Water", *Waters,* Retrieved on May 10, 2019 from
https://www.waterscoaustralia.com.au/pages/why-filter-water,

[2] B.Wolff-Reichert, "A Conceptual tour of PNMR" (TeachSpin, Buffalo, New York, 2010).

[3] "Pulsed/CW NMR Spectrometer, PS2-A INSTRUCTOR'S MANUAL", (TeachSpin, Buffalo, New York, 2010), Rev 1.4.