Anup Mishra

Testing the Efficacy of The Prototype Water Purification System for Shower Water

Helsinki Metropolia University of Applied Sciences

Bachelor's Degree

Environmental Engineering

Thesis

Date: 08/05/2015

Abstract

Author(s)	Anup Mishra
Title	Testing the Efficacy of the prototype water purification system for shower water
Number of Pages	62 pages + 7 appendices
Date	24 April 2015
Degree	Bachelor of Engineering
Degree Programme	Environmental Engineering
Specialisation option	Renewable Energy
Instructor(s)	Juhatuomas Vuorisalo, Thesis Supervisior Marjut Haimila , Lecturer Johanna Kortesalmi, Laboratory Instructor Minna Paananen- Porkka , Language Advisor

The purpose of the thesis was to study the prototype shower water purification system. The chemical analysis was done to check the removal efficiency and overall efficacy of the product and the impact of shampoo in the process.

An experimental design was then devised with 54 samples (27 before and 27 after) all together. Three different concentration of shampoo 5 ml, 10ml and 15 ml were used to study the effect of shampoo in the process and to determine the efficiency process. Each concentration had 3 batches with 3 replicates. pH, calcium, magnesium, potassium, turbidity, surface Tension, fluoride chloride, phosphate and sulphate were measured with the help of different measuring equipment. The major application of the thesis will be in the small water purification system for individual homes and especially in the usage of activated carbon and sand as an effective measure for the purification system.

pH was measured with a pH meter, Ca, Mg and K were measured with the Atomic electron spectroscopy, turbidity was measured with turbidity meter, surface tension by Tensiometer and F, Cl, PO_4 and SO_4 were measured by Ion Chromatography. The experiments were performed in the Helsinki Metropolia UAS laboratory, while sampling was done in Vantaa.

Of the results analysed, the process had the highest average removal percentage for turbidity (98.8 %) while chloride removal was 55.89 %, fluoride removal was 46.28 % and calcium removal was 34.06 %. The average conductivity and sulphate removal were 13.6 % and 11.6 % while some elements had their amount increased, for instance in case of potassium (370.09%), surface tension (136 94 %) and phosphate (66.17 %). Magnesium and pH rose by 39.05% and 12.86 % respectively.

The analysis of the results with ANOVA and box plots showed the effect of concentration and batches concentration interaction for all of the elements along with their batches. It also suggested that the process set up was quite good for majority of the elements tested and ready to install with only two element exceeding the drinking water quality levels while further research was needed in the field of activated carbon and the use of other chemicals to precipitate the excess phosphates.

Keywords	Shower loop, Ion chromatography, pH, AES, Turbidity, Con-

	ductivity, Surface tension, water processing, activated carbon, sand, efficacy, ANOVA, box plots, SNK, C test

Contents

Appendices

Acknowledgment

My utmost gratitude goes to Juhatuomas Vuorisalo for being my thesis supervisor and to Jason Selvarajan for providing me this thesis topic and work in his development project. I cannot thank enough for Jason's help and support in every step during my internship and thesis. I have to also thank for him for giving me an opportunity to present his ideas and present Shower Loop in Copenhagen, Denmark.

There are few more people that I would like my express deepest respectto . First and fore-most, lecturer Marjut Haimila for her immense support and patience when I was doing the laboratory analyses. Secondly, I wish to thank our laboratory instructor Johanna Kortesalmi for helping me with the Atomic Electron Spectroscopy and my language instructor Dr. Minna Paananen Porkka. My special regards to Veera Udd for her moral support in times of need. I would also like to thank Dr. Veli-matti Taavitsainen and Bipin Dulal for their amazing support in analysing the data.

I would also like to thank my parents ,Rajendra and Radhika Mishra, and to my friends, Roshan, Rupesh and Suman, who help me in the completion of this thesis and always keep me motivated.

Finally, this thesis is dedicated to all the victims of the massive earthquake in Nepal.

Abbreviations

UV-C	Ultraviolet Radiation Subset C
Ca	Calcium
K	Potassium
Mg	Magnesium
ph	Phenopthalein
IC	Ion Chromatography
LC	Liquid Chromatography
AES	Atomic Electron Spectroscopy
SO_4	Sulphate
PO_4	Phosphate
F	Flourine
Cl	Chlorine
NTU	Nephelometric Turbidity Unit
USGS	United States Geological Survey
USEPA	United Statesenvironment Protection Agency
UAS	University Of Applied Sciences
ANOVA	Analysis Of Variance
H0	Null Hypothesis
H1	Alternative/ Research Hypothesis
$CaCl_2.2H_2O$	Calcium chloride
KNO_3	Potassium nitrate
$MgCl_2.6H_2O$	Magnesium Chloride Hexahydrate
$Na_2SO_4.10H_2O$	Sodium Sulphate Decahydrate
NaCl	Sodium Chloride
$Na_3PO_4.12H_2O$	Sodium Phosphate Dodecahydrate
NaF	Sodium Fluoride
T	Trial
R	Replicate

List of Figures

Appendices

List of Tables

Appendices

1 Introduction

Water is essential to life on our planet. This fundamental resource is of such importance because no living organism can survive without water. Throughout the world, water is recognized as the most fundamental and indispensable of all natural resources and it is clear that neither social and economic development, nor environmental diversity, can be sustained without water. (Kupchella and Hyland, 1993). Therefore, any solutions to decrease the usage of water and reuse is of high importance.

Water supplies continue to dwindle because of resource depletion and pollution, while demand is rising fast because population growth is coupled with rapid industrialization, mechanisation and urbanisation. (Gleick, 1986). The situation is particularly acute in the arid regions of the world where water scarcity and associated increases in water pollution are closely linked to the prevalence of poverty, hunger and disease. (Nkwonta et al., 2010)

The reuse of water, including domestic and industrial waste waters is not a new concept. The indirect reuse of water happens all the time in nature as we have been using the same water which have been once used in domestic/ industrial purposes and later on discharged into fresh or underground water. Throughout the world underground water have been reclaimed for irrigation purposes for many years. There are also an increasing number of recycling methods for water used in swimming pools, and ground water recharge. Industries frequently use the waste waters for cooling, quenching and washing operations.

In considering the subject of water reuse, the term “water reuse” can be differentiated with “water recycle”. While water reuse refers to the reclamation of wastewater and its subsequent use in different purposes, water recycle involves using reclaimed water for the same purpose. The prototype shower water system, is thus, an example for water recycling system. (Engelbrecht, Richard.S, 1986)

The use of activated carbon filters has been for centuries now and still there are numerous researchers investigating the possibilities and new applications. The target of these experiments is to give an insight to the usefulness of those filters to the system. There were altogether 6 tests performed with the soap water solution and the data was thoroughly examined. All of the tests were performed in the laboratory of Helsinki Metropolia University of Applied Sciences, Myyrmäki Unit.

2 Objectives

The reuse and recycling of water is of high priority and can significantly reduce the water foot print. Also, it will be cost effective for the people to reuse the same water. As to the shower loop, it saves both water and money. In addition to this, reuse of grey water would eventually help reduce the environmental impact of natural fresh water like rivers and lakes.

The objective of this thesis is to develop, test, and refine a shower recycling system for domestic use, mainly in residential builindings, small cottage houses and also to any region where water is scarce.

The specific objectives of this thesis are as follows:

1. To research about activated carbon, experimental methods, and the elements to be tested.
2. To conduct laboratory tests on the prototype shower wastewater recycling system.
3. To create sample shower water with different concentrations of shampoo. The sample shower water would not contain any other contaminants other than shampoo and would then be ran through the process.
4. To confirm that the wastewater effluent from the portable bath unit used can be treated by the existing system, mainly by carbon filters in order to meet the standard for water that meant for shower reuse.
5. To modify the treatment process as necessary to meet the above criteria.
6. To perform chemical analysis of the waste shower to identify and quantify contaminants that may have potential health implications.
7. To conduct chemical analyses by measuring pH, conductivity, turbidity, and the amount of calcium, magnesium, potassium, fluoride, chloride, and sulphate and phosphate levels.
8. Perform data analysis to see what affects the process, mainly concentration and the interaction effect on the measurement.
9. To compare the quality of the process water to drinking quality standards and to previous results.

3 Literature Review

3.1 Shower loop

Showerloop is a process designed and developed by Jason Selvarajan and Keiran Holland in 2013. It was designed to reduce the ecological impact of showers by filtrating, sterilizing and recirculating shower in real time, thus significantly reducing the amount of water and energy required to enjoy a warm shower. The process is different to that of normal showers as it recycles the water in real time by using carbon and sand filters along with UV-C. Sand and granular activated carbon filters are utilised to clean the water, after the water is disinfected with ultraviolet subset c radiation or UV-C. There are number of sensors like a temperature sensor, flow sensor and a timer to keep the user up to date with the ongoing process. The process saves about 90 % more water and 70 % more energy than the normal shower thus being more sustainable to use. (Selvarajan.J, and Holland K, 2014). Figure 1 and figure 2 show the prototype shower loop with the existing automation on top.

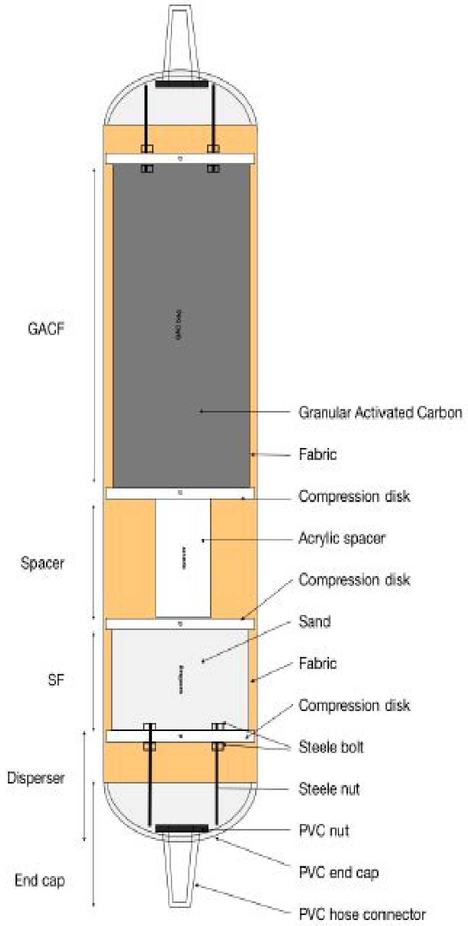


Figure 1. Unscaled assembled diagram of the water filter with sand and granular activated carbon airbags

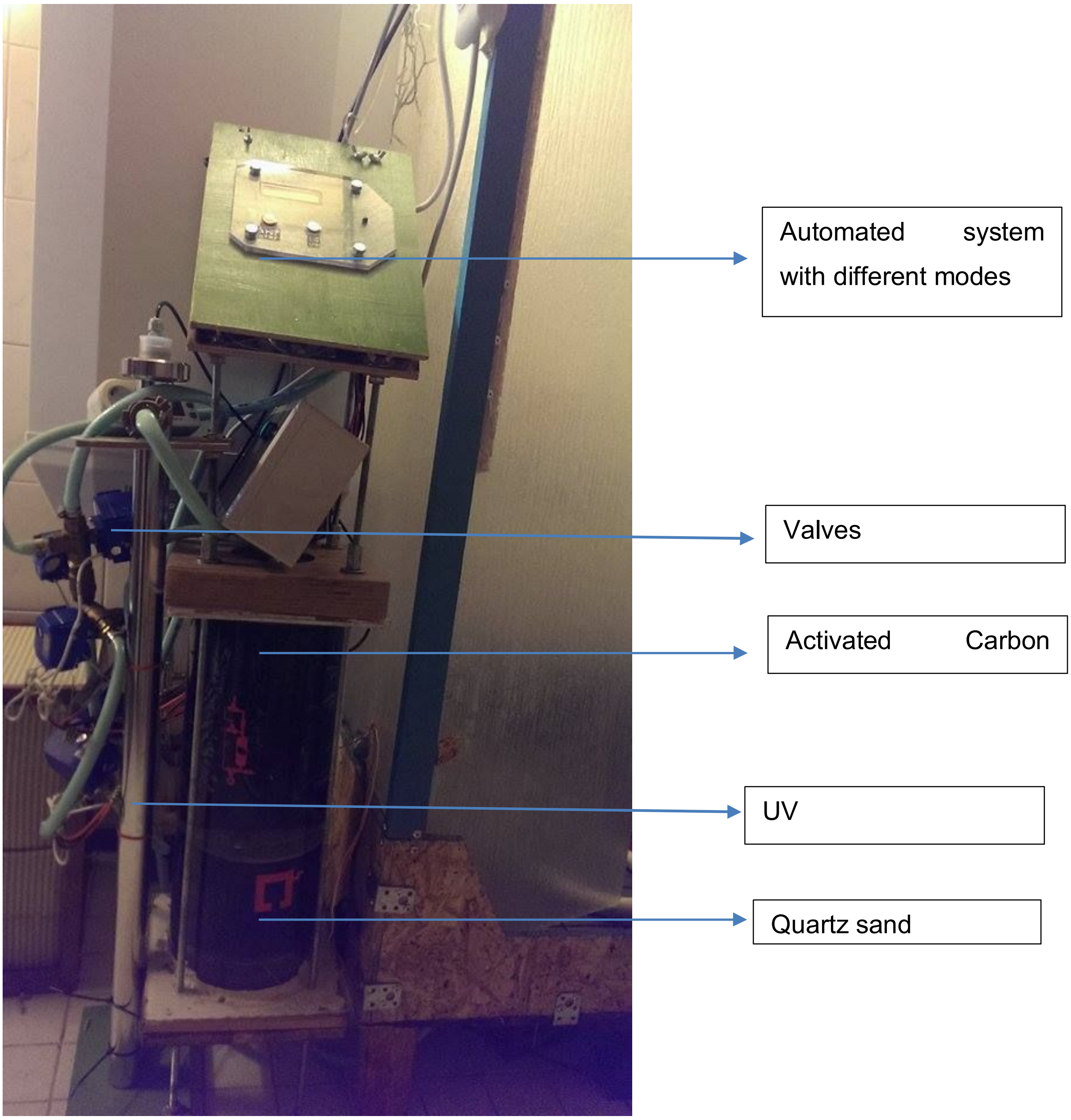


Figure 2. Shower magic prototype with automation

3.1.1 Working condition

Shower loop is a simple shower water purifying process with loads of advantages which one can install in an existing shower room. When one gets into the shower, it runs in the same way as the normal shower, but the major difference is that the water that passes away from ones' body gets cleaned by various filters and reappears through the shower head. The settings like temperature, flow rate, and even the lightings can be set by the user. Once ready with the shower, the user presses the backwash mode wherein the water changes the direction. The user can also change to bypass mode if he/she do not want to recycle the water.

The shower also allows the user to have a fixed shower time for instance 2-minute or 5-minute or can even be longer. It also notifies the user about the usage of its filter system and suggests when to change it.

3.1.2 Parts

Shower loop contains 5 different types of filters: gravity, microfiber, sand, activated carbon and UV-C. Each of them helps to make the water cleaner, bacteria free and even safe to drink. (Selvarajan J and Holland,K, 2014). The main element is the activated carbon, which removes most of the surfactants and particles away.

3.1.3 Modes

The shower loop has 3 different modes from which user can choose the preferable one.

The one that accounts for the saving of the water and electricity is the **Shower mode** (in the figure 3 as shower magic) wherein the shower water recycles and goes to shower head. The other two modes are **Back wash mode** which simply changes the direction of the flow of the water and clears any major matters stuck in the carbon filters or the sand. The water is not recycled in this mode whereas in **Bypass mode** the water is allowed to bypass the filtering system entirely and it is suggested to be used after every shower taken so as to enhance the working days of the activated carbon as well as other materials used in the system.

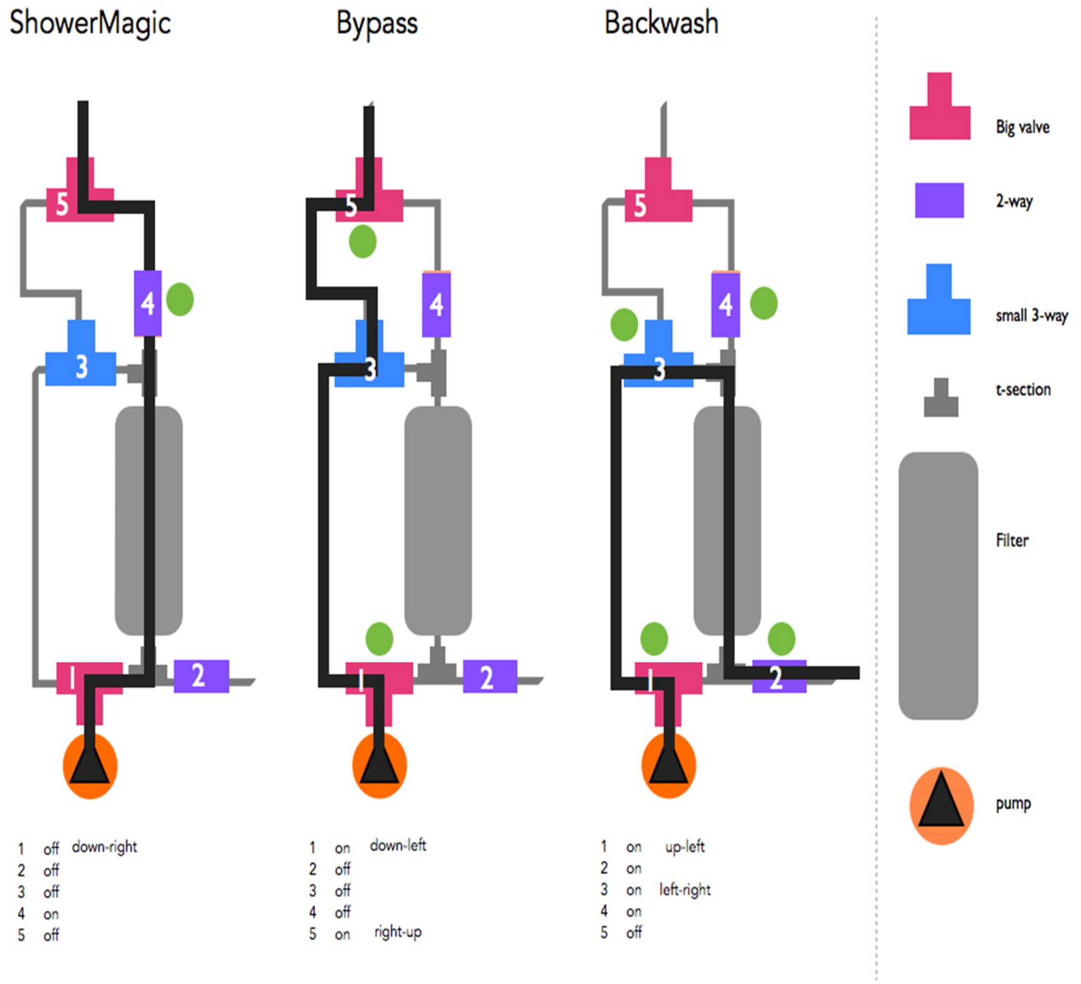


Figure 3. Different modes of Showerloop with the valves

Figure 3 illustrates the different modes of the Showerloop with different kind of valves and their opening and closing stages.

3.2 Activated carbon

Active refers to adsorption activity: a carbon that is activated has a high capacity for adsorption. The carbon may be produced from any source, including vegetable, animal, petroleum, coal and peat. It is believed that many different oxygen-based acidic functionalities are present on the surface of activated carbon. These include carboxyl group, phenolic hydroxyl, quinone-type carbonyls, lactones, carboxylic acid anhydrides, ethers and cyclic peroxides. Such groups affect the acidity and the mechanism of bonding and surface catalysis. (Van Winkle, 2000)

3.2.1 Manufacture

Activated carbon is manufactured in different ways and their chemical and physical properties depend on the source material and manufacturing process. Most of the variability is caused by the source materials which differ profoundly in their structure and chemical composition. Coconut shells, a popular source for ac, are used in gas phase applications, produces a uniformly porous material with high percentage of micropores. Carbons produces from hardwood are noted for their greater variability in pore size with a larger percentage of mesopores. Likewise, bone char, peat petroleum and coal have different structural properties, and would result in variable performance even if the manufacturing technique was same. (Mattson, Mark, 1971)

There are mainly two categories for the production of activated carbon (ac), high temperature (700+ °C) and employs steam or CO_2; and chemical systems which dehydrate the feed stock. Each method has its own advantages and disadvantages. The chemical technique gives very high yield of an extremely adsorptive material, but requires further strengthening. (Van Winkle, 2000). In case of soft coals and certain other feed materials, a pulverizing stage is necessary to obtain desired material properties. A two stage process may be employed in a controlled atmosphere furnace with a fixed bed or a fluidized bed which results in a more uniform activation. The initial stage is a carbonization step taking place in pyrolysis followed by selective oxidation with steam air or flue gas. The temperature could be in the range of 230 – 700 °C depending on the raw material and desired product. The second stage ranges from 700 - 1000°C in the presence of air. The first stage removes volatiles and inorganics while the second stage results in a minimum of surface oxidation and maximum surface area. (Mattson, Mark, 1971)

The activate carbon used was “STORMS” bio carbon (figure 4). The technical details of the ac are listed below:
Particle size: 0.4 -0.85 mm
Density: 0.46-0.48 g/cm3
Adsorption: 1150m2/g
Bag length =19 cm*30 cm

Figure 4. Activated carbon used in the system

3.3 UV and Quartz sand

The main function of UV is to kill any bacteria or micro-organisms formed in the process cycle. Since, the water may contain bacteria and the formation of bacteria in ac as well as sand, it is essential to have UV to kill any such micro/organisms. The previous tests concluded that the reduction in bacteria via the usage of UV were significant with a removal efficiency of 99%. (Selvarajan, J and Holland. K, 2014). Purion 2500 90W is used in the system, however, it was not used in the experiments in this thesis.

Quartz sand is used in many water filtration processes and it is used to remove common solids found in grey water. The sand however cannot filter the microorganism as they are too small. The relative sizes of some common solids are found in Table 1.

Table 1. Relative particle sizes for common solids found in grey water

Particle	**Size**
Tables salt	100
Human hair	40-70
Skin cells	33
Talcum powder	10

Particle	Size
Fine test dust	0.5

Showerloop has been fitted with quartz sand from Nissilä (sibelco Nordic), which was mesh screened to 250-500 µm. The bag length was 19 cm in diameter * 10 cm in length.

3.4 Water quality standards

The water quality standards are determined by the authorities and are subjective to the country’s internal regulations. The framework however is the same and is given by European Directives. Some European countries are similar with respect to their internal laws or standards, while some are different. The water quality standards are divided to drinking water quality and shower water quality and have their own measurement standards.

3.4.1 Drinking water quality

The quality of drinking water can be influenced by the durability of the metallic, cement-based, and network materials from plastic since these are subject to corrosion and dissolution. Parameters affecting the technical quality of drinking water are for example pH, hardness, and alkalinity, amount of chlorides and sulphates and electrical conductivity. The parameters that reflect the aesthetic quality of drinking water include odour, taste, turbidity and colour as well as levels of iron and manganese. (Mäkinen. R, 2008)

Table 2. Requirement and guide values defined in the Finnish decree on drinking water (Mäkinen, R, 2008)

Parameter	Parametric value	Unit	Requirement, guide value or limit value
Chloride	250	Mg\l	Guide value
Conductivity	2500	µS cm-1 at 20 °C	Guide value
Sulphate	250	Mg\l	Guide value
Turbidity	Acceptable to consumers and no abnormal change		

Parameter	**Parametric value**	**Unit**	**Requirement, guide value or limit value**
Fluoride	1.5	Mg\l	requirement
pH	6.5-9.5		Guide value
Phosphates			No limit value
Calcium			No limit value
Magnesium			No limit value

3.4.2 Adverse effects of contaminants

The adverse effects of the contaminants are tabulated below in Table 3. The contaminants are the ones that have been monitored in this thesis.

Table 3. Effects of contaminants (Ritter. J, 2010)

Contaminant	**Adverse effect**
Chloride	Causes taste. Adds to total dissolved solids and scale. Indicates contamination. Can accelerate the corrosion of some metals.
Colour	Indicates dissolved organics may be present which may lead to trihalomethane formation. Unappealing appearance
Fluoride	Dental fluorosis (mottling or discoloration of teeth)
Odour	Unappealing to drink. May indicate contamination.
pH	Below 6.5, water is corrosive. Above 8.5, water will form scale, taste bitter
Sulphate	Has a laxative effect

3.4.3 Shower water quality

The shower water quality differs from the drinking water quality in that there are many unwanted chemicals and surfactants. The shower water quality also depends on the type of substances used to make the shower system as well as on the products used to washing the hair and body.

Table 4. Shower water quality (Engelbrecht, Richard S, 1986)

Product	**Concentration mg/l**
Silica Flour	100-210
Sodium Chloride	60-180
Castor Oil	20-130
Isopropyl Alcohol	18-105
Ethanol	15-85
Kaolinite	20-50
Oleic Acid	16-50
Talc	41
Tallow	13-38
Stearic Acid	11-31
Coconut Oil	9-30
Castor Oil.Sulfonated (75%)	6-30
Ultravet 60-L	5-25
Ammonium Lauryl Sulfate	5-25
Sodium Lauryl Sulfate	5-22
Epithelium Cells	18
N-N-Diethyl-N-Toluanide	1-15
Sodium Dodecylbensenesulfonate	3-13
Sodium Tripolyphosphate	5-11
Olive Oil.Sulfonated (75%)	2-10
Tannic Acid	1-8
Triethanolamide Alkylbenzene Sulfonate (60%)	1-7
Potassium Olate (20%)	1-6
Kaloin, Colloidal	5
Lactic Acid	5
Triethanoamine	1-5
Urea	1-3
Glycerol	1-3
Potassium Hydroxide	0.7-3
Zinc Stearate	3
Coconut Diethanolamine (92%)	0.5-3
Hair	2
Mineral Oil	0.5-2
Potassium	1.5
Calcium Carbonate	0.9
Aluminium Hydroxide	0.9
Sorbitol	0.7
Dicalcium Phosphate	0.6
Sodium-Ortho-Phenylphenolate	0.6

Product	Concentration mg/l
Sodum-4-Chloro-2-Phenylphenolate	0.5
Sodium Metahosphate	0.4
Aluminium Formate Solution	0.4
Propylene Glycol	0.3
Tricalcium Phosphate	0.2
Volatile Silicone	0.2
Tegacid	0.2
Aluminium Chlorhydrate	0.2
Tween 80	0.2

4 Theory

4.1 pH

pH is related to the concentration of the hydrogen ion and the acid dissociation constant. pH is an indirect measurement of the strength of an acid or base. In aqueous solutions the strength of acids and bases is measured relative to the conjugate acid-base system of H_2O. An acid dissolved in H_2O will increase the concentration of H^+. The pH for pure water is between 6.5 -9.5 (Table 2). An increase or decrease in the pH levels suggests the change in the other elements of the system such as sulphates, or phosphates. For any water quality judgement pH is the very basic element to be tested. pH can values for some of the solutions can be seen in Figure 5.

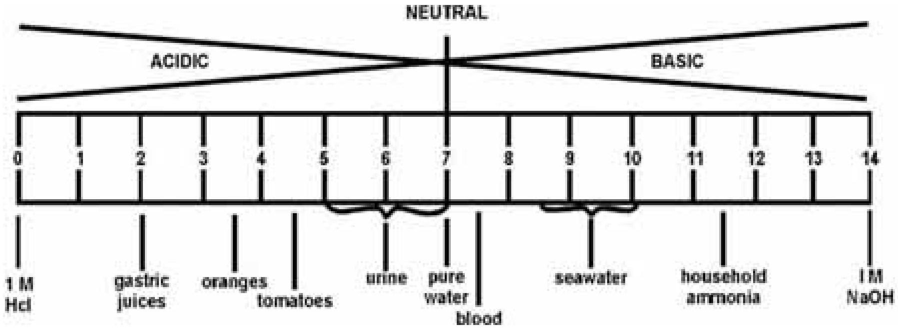


Figure 5. pH measurement scale for some common liquids (water.epa.gov, 2015)

pH is measured by a pH meter which measures the electric potential (millivolts) across the electrode when immersed in water. The electric potential is a function of the hydrogen ion activity in the sample. Therefore, a pH meter can display results in either milivolts (mV) or pH units.

A pH meter consists of a potentiometer, which measures the electric current, a glass electrode, which senses the electric potential where it meets the water sample, a reference electrode, which provides a constant electric potential and a temperature compensating device, which adjusts the readings according to the temperature of the sample. (water.epa.gov, 2015)

4.2 AES

AES or Atomic Emission Spectroscopy is an analysis method to determine the quantity of an element in a sample by using the intensity of light emitted from a flame, spark or arc.

Figure 6. Agilent 4100 MP-AES machine

The Agilent 4100 MP-AES is a new atomic emission spectrometer that features a microwave plasma as the emission source (Figure 6). The source is sustained with nitrogen gas, avoiding the need for more expensive flammable and oxidizing gases used in traditional flames. The spectrometer can also be added to a pneumatic nebulizer, improved trace element detection like selenium.

Elements tested by AES were Calcium (Ca), Magnesium (Mg) and Potassium (K). Each of the elements reacts to different set of wave length thus giving the concentration for each of them. Table 5 presents the results.

Table 5. AES results for calcium, potassium, and magnesium.

Elements	**Wavelength (nm)**
Calcium	393.666
Potassium	766.491
Magnesium	285.213

4.2.1 Working principle

The nitrogen gas is used as the plasma gas that gives a robust plasma with a conventional torch. Nitrogen can be supplied either via bottled gas or via air generator. Magnetic excitation gives a toroidal plasma and effective central zone for sample injection. The microwave then magnetically excites nitrogen plasma which in turn provides a robust, high temperature source and a cooler central channel suitable for sample atomization.
The high intensity atomization lines are then detected by the monochrome detector and displayed in the screen (Figure 7).

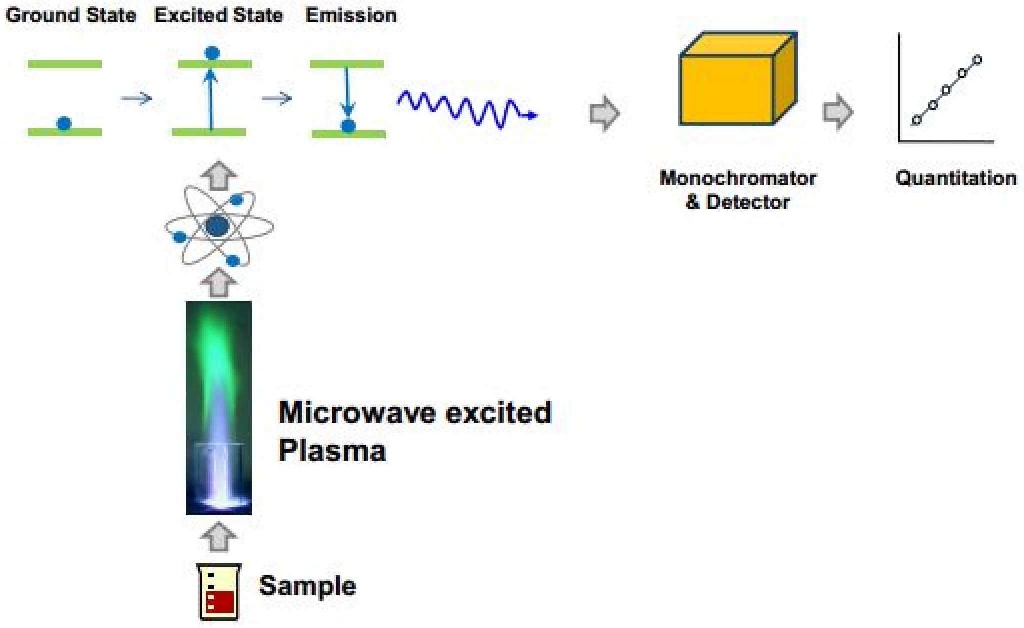


Figure 7. Microwave plasma emission (Shrader et al., 2011)

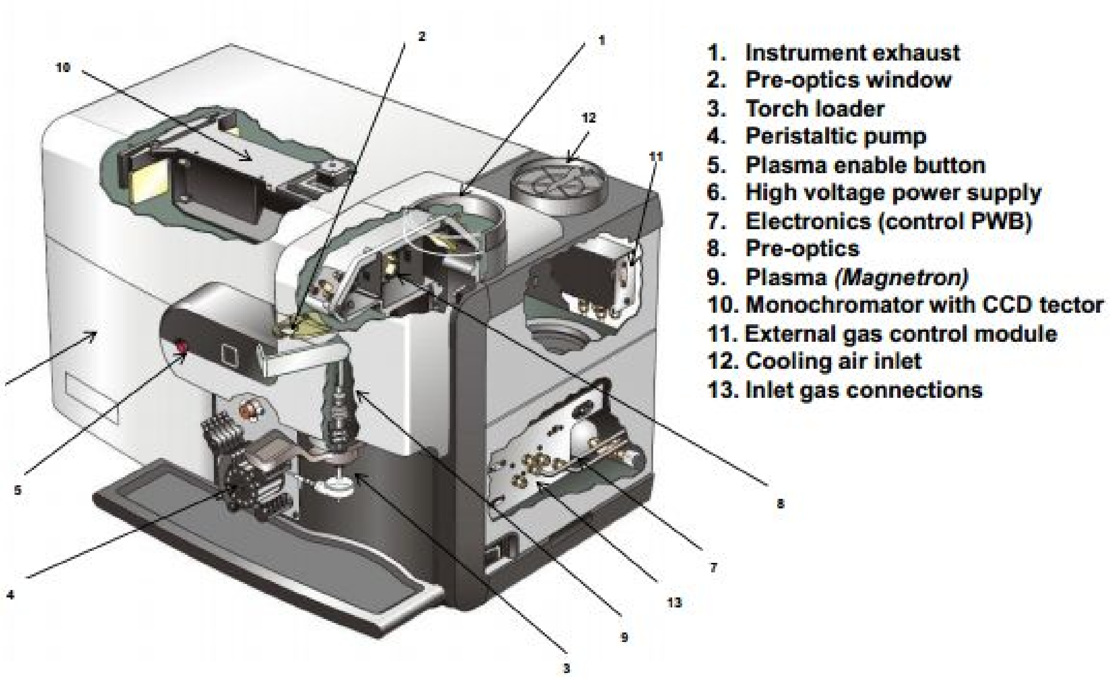


Figure 8. Schematic diagram of MP-AES (Shrader et at.,2011)

The schematic diagram can be seen in Figure 8, showing the inside parts of the MP-AES 4100.

4.2.2 Mother solutions

The mother solutions needs to be created for each of the measured elements and are usually measured as 1000mg/l. Since, 3 elements were detected by AES, 3 standard solutions had to be created. Table 6 displays the original compounds, molecular mass and the amounts taken for 1000 mg/l.

Table 6. Mother solutions of the measured elements.

Elements	**Original Compound**	**Molecular Mass**	**Amount to be made as 1000mg/l**
Calcium	$CaCl_2.2H_2O$	151.3016	3.775
Potassium	KNO_3	101.11	2.586
Magnesium	$MgCl_2.6H_2O$	203.30	8.364

4.2.3 Standard solutions

From each of the mother solution, 5 different standard solutions were created (Table7). The range of concentration of the standard solutions differed because of the predicted amount of elements in the samples.

Table 7. Standard solutions of the measured elements.

Elements	**Standard solutions (mg/l)**
Calcium	10, 25, 50, 85, 100
Potassium	10, 30, 50 70 ,100
Magnesium	1,3,5,7,10

4.3 Conductance

Conductivity of a substance is the ability or power to conduct or transmit heat, electricity or sound. (Lenntech, 2015). Conductivity in water is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulphate and phosphate anions or sodium, magnesium, calcium, iron and aluminium cations. Organic compounds like oil, phenol, alcohol do not affect the electrical conductivity highly whereas temperature is directly proportional to the conductivity. The warmer the water, the higher is the conductivity. (Water.epa.gov, 2015). Electrical conductivity is defined as the ratio between current density and electric field intensity and it is the opposite of resistivity (r, [W*m]):
S= J/e = 1/r (Lenntech, 2015)

Conductivity is measured in mho or Siemens. It can be measured as micromhos per centimetre (μmhos/cm) or micro Siemens per centimetre (μs/cm). Distilled water has a conductivity range of 0.5 to 3 μmhos/cm. Streams have a general range of 50 to 1500 μmhos/cm. Inland fresh waters supporting good aquatic life has a range of 50 to 1500 μmhos/cm. (Water.epa.gov, 2015). More conductivities of water from different sources can be seen in Table 8 in 3 different units of measure.

Table 8. Aqueous conductivities (systems, 2015)

Solution	**μS/cm**	**mS/cm**	**Ppm**
Totally pure water	0.055		
Typically DI water	0.1		

Solution	µS/cm	mS/cm	Ppm
Distilled water	0.5		
RO water	50-100	0.05-0.1	25-50
Domestic “tap” water	500-800	0.5-0.8	250-400
Potable water (max)	1055	1.055	528
Sea water	56,000	56	28,000
Brackish water	100,000	100	50,000

4.3.1 Working principle

Conductivity is measured with a probe and a meter. Voltage is applied between two electrodes in a probe immersed in the sample water. The drop in voltage caused by the resistance of the water is used to calculate the conductivity per centimetre. The meter converts the centimetre to micromhos per centimetre and displays the result for the user. It is vital to calibrate the conductivity meter prior to use so as to minimise the experimental error. The probe should be rinsed properly with distilled or deionized water after each measurement.

4.4 Surface Tension

Surface Tension is a property of a liquid in contact with air or vapour that makes it behave as if it was covered with a thin membrane under tension. For example, if one fills a glass of water and carefully places a thin razor blade onto the surface of the water it would float for a short time due to this pseudo membrane which supports it. This tension at the surface results from the intermolecular forces within the solution that causes the exposed surface to contract to the smallest possible area. The reason being that the interior of a solution interacts with other molecules equally whereas the molecules at the surface of the liquid are only affected by the molecules below it.

Surface tension can also be defined as the force acting over the surface of the solution per unit length of the surface perpendicular to the force. It is usually expressed in milli newtons per meter or in dynes per centimetre. There are various methods to measure the surface tension of the solution; in this thesis, the surface tension was calculated by using tensiometer (Figure 9) through DuNouy ring measurement.

4.4.1 DuNouy ring measurement

The top of Figure 10 shows the various phases in a DuNouy ring measurement.

1. When the ring is above the surface the force is zeroed
2. When it touches the surface the wetting of the ring causes some positive force.
3. Negative force

4-5 Some positive force

6. Force continuing to rise
7. Maximum force
8. Force starts to decrease

Figure 9 shows the tensiometer used to calculate the surface tension. The different phases can also be expressed in a Force vs Time graph can be seen in bottom of Figure 10.

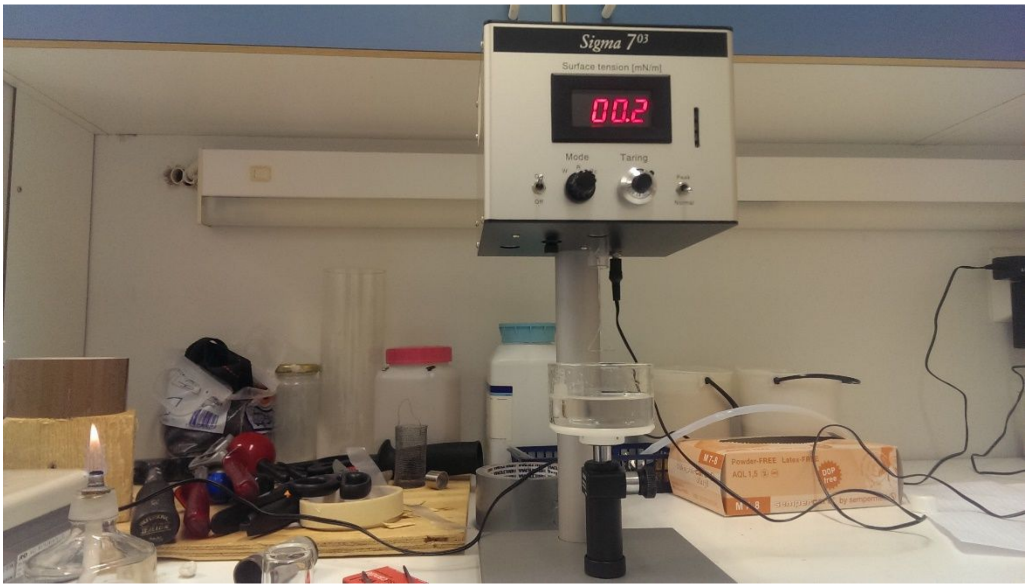


Figure 9. Sigma 700 Tensiometer for measuring DuNouy ring measurement.

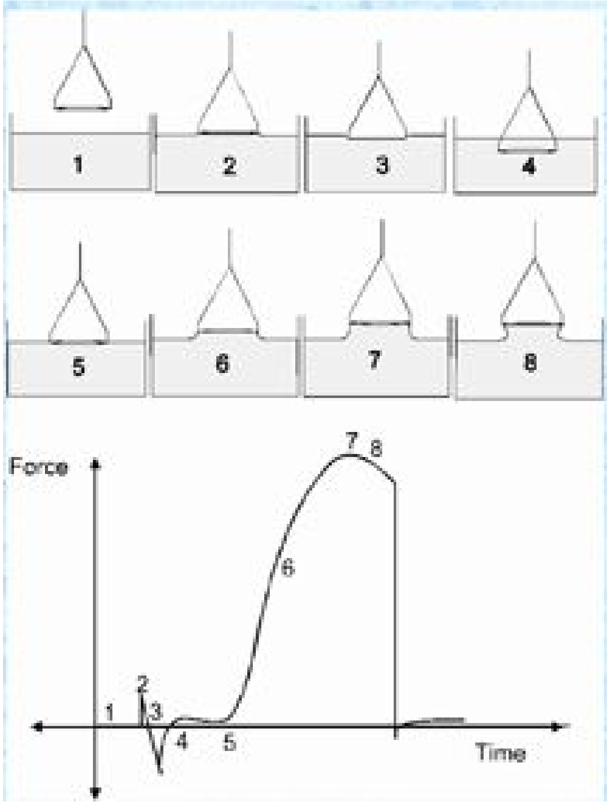


Figure 10. DuNouy ring measurement (Gatenby, A. 2015)

4.4.2 Modes

In this experiment the uncorrected mode R or the corrected mode Rc can be used. In this thesis the uncorrected mode was used and which displays the value as the force per length value (mN/m). The length in this case is the perimeter of the outer side of the ring plus the perimeter of the inner side of the ring. Sigma 703 uses the linear correction model meaning when the surface tension of the water at 20 C is measured a correction factor is applied so that the surface tension value shows 72.8 mN/m. then the actor is applied to all measurements.

4.4.3 Measurement style

The measurement can be done in two different positions, in the normal position or in the peak position. The ring is first hung on the hook and the value of the surface tension is zeroed with the taring knob. By lifting the stage the ring is immersed inside the liquid. In Normal position lowering the stage one is able to find the maximum force directed to the ring thus giving the surface tension. In the peak position, the stage is slowly lowered until the ring breaks out from the liquid from the liquid. The display shows the value of force per length. The peak position was used during this measurement.

4.5 Turbidity

Turbidity is a measure of the degree to which water loses its transparency due to suspended particulates. The more total suspended solids there are in the water, the murkier it seems and the higher the turbidity is. There are various parameters influencing the cloudiness of the water such as phytoplankton, sediments from erosion, re-suspended sediments from the bottom, water discharge, algae growth and urban run-off. The maximum allowed turbidity for drinking water is 1 Nephelometric Turbidity Units (NTU), while up to 5 NTU is acceptable. (Lenntech, 2015). High turbidity can significantly reduce the aesthetic quality of lakes and streams, having a harmful impact on recreation and tourism. It can increase the cost of water treatment for drinking and food processing as well harm another aquatic life. (Pca.state.mn.us, 2015)

Monitoring of filtered water quality by turbidity measurement is routinely carried out in water treatment plants. Originally they were mainly aesthetic reasons- a visibly cloudy or turbid appearance is undesirable, while now the turbidity level can help to determine the presence of different organism and unwanted particles. (Gregory. J, 1998).

4.6 Chromatography

Chromatography is unique in the history of analytical methodology and is probably the most powerful and versatile technique available to a modern analyst. In a single procedure it can separate a mixture into its individual components and simultaneously determine quantitavely the amount of each component present. There could be many complexities in samples including its state or its origin from a single substance or a range of chemical substances.

All chromatographic separations are carried out using a mobile and a stationary phase. As a result of this prerequisite, the primary classification of chromatography is based on the physical nature of the mobile phase. Thus, all separation processes that utilize a gas as the mobile phase are classed as gas chromatography. Conversely, all separation processes that utilize a liquid as the mobile phase are classed as liquid chromatography. (Scott Raymond P.W, 1995). A tabulated list of the different types of chromatographic methods is visible in Table 9.

Table 9. Classification of chromatographic techniques (Scott Raymond P.W, 1995))

Mobile Phase Gas **Gas Chromatography**		Mobile Phase Liquid **Liquid Chromatography**	
Stationary Phase Liquid **Gas-Liquid Chromatography**	Stationary Phase Solid **Gas- Solid Chromatography**	Stationary Phase Liquid **Liquid-Liquid Chromatography**	Stationary Phase Solid **Liquid-Solid Chromatography**

4.6.1 Liquid chromatography

The term *liquid chromatography* encompasses a number of separation techniques with a single common feature, that of a liquid mobile phase. Compared with gases liquids provide a greater variety of solvating capabilities with more scope for selectivity optimization, while gases have more favourable kinetic properties yielding higher efficiencies and shorter separation times. Consequently, separation in liquid chromatography are usually performed with a modest number of theoretical plates at an optimized selectivity achieved by appropriate selection of the separation mode, stationary phase structure, and mobile phase composition. (Colin F. Poole, 2003). Separations using a liquid mobile phase are based on the following four principles: (Kellner R, 1998).

- Adsorption
- Distribution
- Ion exchange
- Exclusion

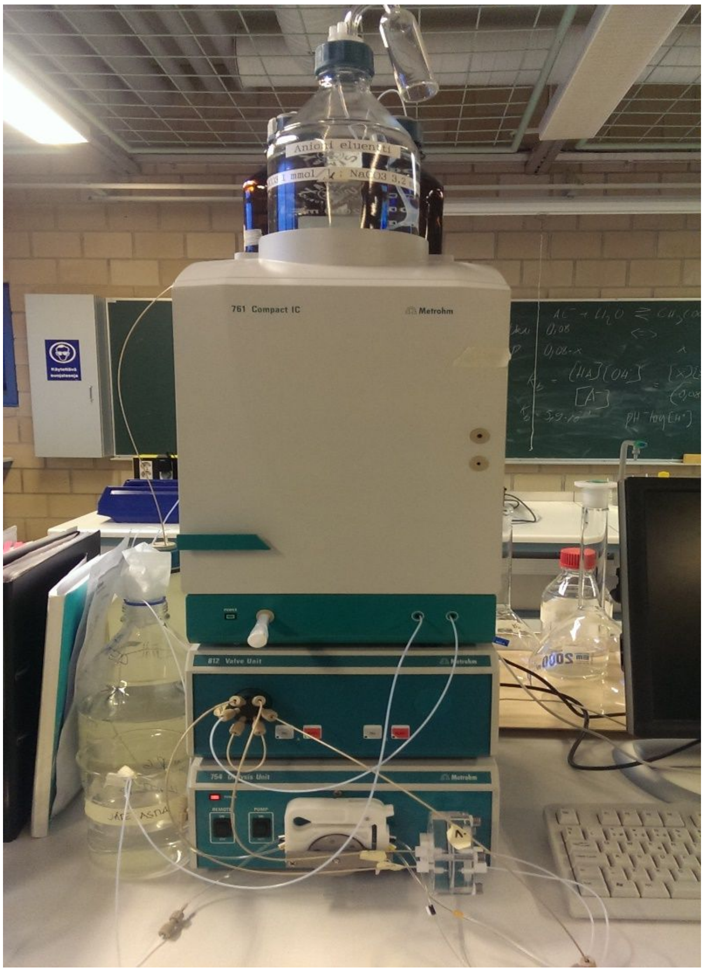
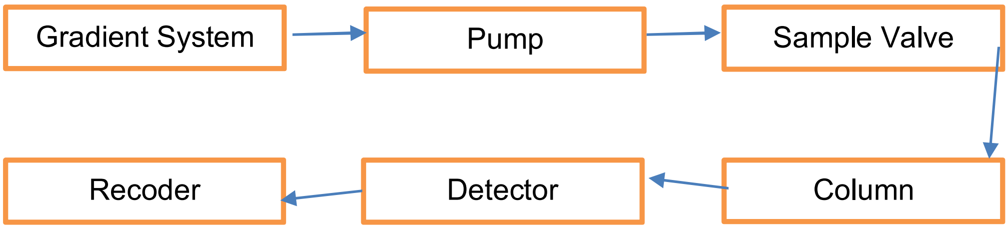


Figure 11. Metrohm IC 761 Ion chromatography instrument

4.6.2 Theory

A sample mixture is composed of different molecular components that have different chemical structures, and to be detectable, each component must have a population of molecules. All of the molecules of a single component have the same chemical structure, and this population is referred to as sample or analyte brand as it moves through the column. The chemical structure of each component determines the strength and type of intermolecular forces it has with the mobile and stationary phase. These intermolecular forces govern the relative strength of analyte–mobile phase and analyte-stationary phase interactions, which determines the relative amounts of the analyte molecules in mobile and stationary phase. If the interactions are strong enough, the analyte molecules will bind or adsorb to the stationary phase. Stronger analyte interactions with the stationary phase increase the fraction of analyte adsorbed to the stationary phase and decrease the analyte velocity. (Brown, P., Grushka, E. 2001)

The basic liquid chromatograph consists of six units, the gradient system, the pump, the sample valve, the column, the detector and the recorder. (Figure 12)



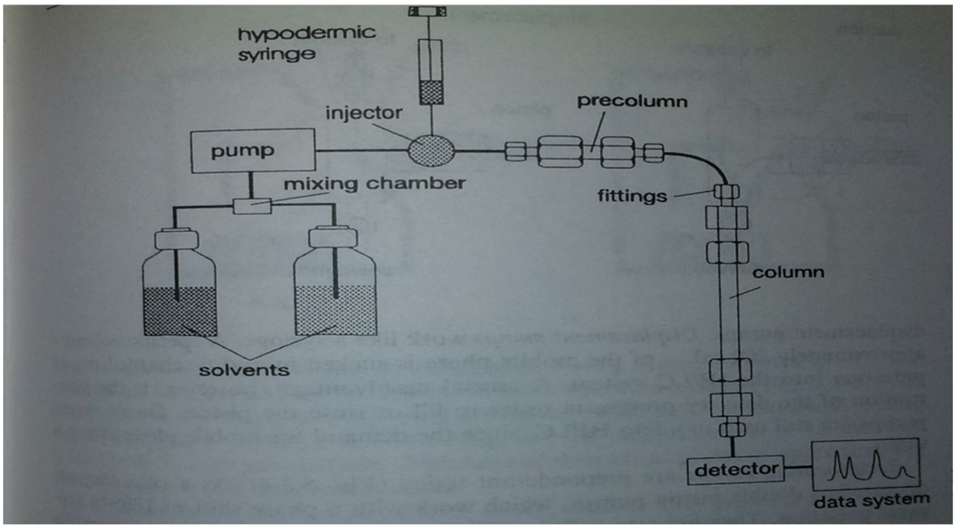


Figure 12. Structure of a HPLC unit with precolumn (Kellner. R, 1998)

4.6.3 Gradient system

The gradient system can vary from a simple glass reservoir for isocratic development to a two or three solvent programmer. Solvent reservoirs should be fitted with a device to allow helium to be bubbled through the solvent to remove dissolved oxygen and nitrogen. The presence of dissolved air can cause bubbles to form in the mobile phase during passage through the column and reduce efficiency. In other cases, it might also result larger noise in the detector systems. (Scott Raymond P.W, 1995). The simplest way to clean the solvents for this is by sucking them through a Millipore filter under vacuum. The dissolved gases, such as nitrogen and oxygen, can also be out gased by introducing a noble gas like helium or by being processing in an ultrasound bath. (Kellner, R, 1998). The solvents used as mobile phase are stored in a reservoir in glass or stainless steel bottles (Figure 13).

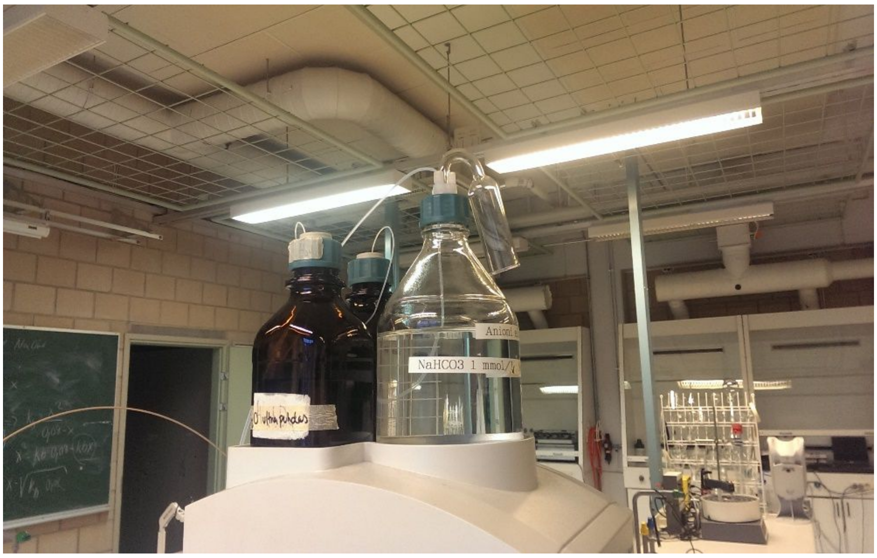


Figure 13. Solvents (Eluent, Water, and Sulphuric acid solutions)

4.6.4 Pumps

LC pumps have evolved over the ages and there are now a number of types available depending on the separation techniques. The first two high pressure pumps to be utilized were syringe pump and pneumatic pump. However, other types like diaphragm pump and rapid refill pump are also being used extensively. (Scott Raymond P.W, 1995). In metrohm IC 761, a syringe pump is used while there is also presence of peristaltic pump. To protect the pumps, pulsation dampener is used which reduces interfering pulsation in highly sensitive measurements and also protect the column material against pressure shock caused by the injection. (Metrohm)

To protect the pump against foreign materials, the eluent is passed through microfiltration (0.45 µm). Salt crystals between the piston and the seal are abrasive particles that causes contaminated valves, pressure rise and in extreme cases scratched pistons. Thus, it is vital to keep to ensure that no precipitate can appear.

4.6.5 Columns

The column is the key component of an LC system, because the attainable quality of IC depends to a large extent on the separation efficiency of the column used and holds the stationary phase. The choice of stationary phase is of critical importance, because the stationary phase largely determines what molecular properties the separation will be based on. (Brown, P., Grushka, E. 2001). The columns may differ as to the type of IC and to capacity factors, selectivity, plate number and resolution. To avoid contamination by abrasive particles arising from piston seals of the high –pressure pump, an in-linefilter between pump and injection valve can be used. The readily interchangeable pre-columns protects the actual separating column and increases the service life. (Metrohm)

In Metrohm IC 761 the column used is Polyvinyl with quaternary ammonium groups (Figure 14), which is suitable for separation of neutral and ionic compounds. The size of the column 4 *100 mm with the particle size 5 µm.

Figure 14. Metrohm IC 761 column

4.6.6 Detector

A Chromatography detector is a device that locates the dimensions of space or time, the positions of the components of a mixture subjected to a chromatographic process and allows the senses to appreciate the nature of the separation obtained. Vast majority of the LC are monitored by mainly four detectors the electrical conductivity detector, the refractive index detector, the fluorescence detector and the UV detector. (Scott Raymond P.W, 1995). In metrohm IC, a conductivity detector with temperature stability is used. The detector temperature varies by less than 0.01 °C and can be optimally adapted to the ambient conditions. (Metrohm). The electrical conductivity detector (Figure 15) is used extensively in ion exchange chromatography.

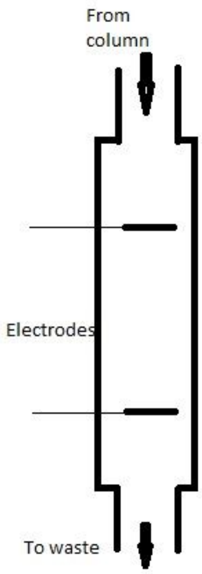


Figure 15. The Electrical conductivity detector

It can be clearly seen that the basic sensor is very simple and can be designed to have effective sensing volume of a few nanoliters.

4.6.7 Mother solutions

The mother solution were created from different compounds and from that 5 standard solutions were prepared. Table 10 displays the elements and the compounds with their molecular weight and the weighted amount taken. The standard solutions were 0.5 mg/l, 2 mg/l, 5mg/l, 10 mg/l and 20 mg/l.

Table 10. Compounds used for standard solution for Ion Chromatography.

Elements	Original Compound	Molecular weight of original compounds(g)	Molecular weight of measured compounds (g)	Amount(g) to be made as 1000mg/l
Sulphate	$Na_2SO_4.10H_2O$	322.19	96.062	3.353
Chloride	NaCl	58.44	35.453	1.648
Phosphate	$Na_3PO_4.12H_2O$	380.12	94.9714	4
Fluoride	NaF	41.989	18.998	2.21

4.6.8 Eluents

The eluent prepared for the experiment was 3.2 mmol /l Na_2CO_3 with 1 mmol /l $NaHCO_3$. Since, the eluent was prepared in 2l bottle, the results were doubled.
The following formula were used in the calculations.

Number of moles (n) = $\frac{mass\ (m)}{molar\ mass\ (M)}$

Mass (m) = n *M

Thus, for the amount of Na_2CO_3, needed was calculated as follows;

Mass (m) = 0.0032 mol * 105.99 g

=0.339 g/l

For 2 l = 2*0.339 = 0.6784 g /2l

Similarly, the amount of $NaHCO_3$, needed was calculated as follows;

m= n*M

m= 0.001 mol *84.01 g

m= 0.08401 g/l

For 2 l,

=2 * 0.08401 = 0.16802 g/2l

Compounds	**Number of moles (n)**	**Mass (m)**	**Molar mass (M)**	**Amount for 2 l (g)**
Na_2CO_3	0.0032	0.339	105.99	0.6784
$NaHCO_3$	0.001	0.08401	84.01	0.16802

5 Approach and Sampling

5.1 Preliminary testing

According to US EPA, 2011, the average usage of shampoo was found to be 11.76 ml per use. Thus, the initial sampling and experiment was performed with different levels of concentration and types of shampoo. A total of 3 types of shampoo, B, C, and D were used with 5 different concentration levels (3, 5.5, 8, 10.5, 13, 15. 5) ml per 8 litre. The tests were carried in the Myyrmäki lab unit and even though these tests were carried without any replicates, the data was studied to see the range of the elements before and after the process.

5.2 Final experiment

The final experiments were done after the preliminary results were obtained, and a design matrix was developed to understand the process efficiency. An experimental set up was designed with the lowest concentration of X shampoo was set as 5 ml and the highest as 15 ml.

The sampling was done by designing the experiments with 3 replicates:

```
Stage=rep(c(0,1)3)
Concentration=rep(c(5,10,15)3)
Design.M =expand.grid(Concentration, Stage)
Design.M
```

Table 11. Number of batches and replicates for the experiment

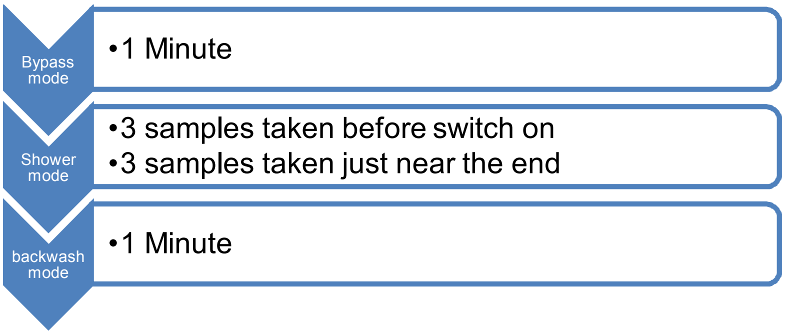
Sample	Conc	Stage
1	5	0
2	10	0
3	15	0
4	5	0
5	10	0
6	15	0
7	5	0
8	10	0
9	15	0
10	5	1
11	10	1
12	15	1
13	5	1
14	10	1
15	15	1
16	5	1
17	10	1
18	15	1
19	5	0
20	10	0
21	15	0
22	5	0
23	10	0
24	15	0
25	5	0
26	10	0
27	15	0
28	5	1
29	10	1
30	15	1
31	5	1
32	10	1
33	15	1
34	5	1
35	10	1
36	15	1
37	5	0
38	10	0
39	15	0
40	5	0
41	10	0
42	15	0
43	5	0
44	10	0
45	15	0
46	5	1
47	10	1
48	15	1
49	5	1
50	10	1
51	15	1
52	5	1
53	10	1
54	15	1

This gave the total number of samples to be taken from the process with the different concentrations 5, 10 and 15. The total number of samples was equal to 54 with 18 samples to be taken from each concentrations. Due to lack of resources, the experiments were done in 3 phases. The first experiment performed was with concentration 5 ml on November 24, 2014 and then 10 ml on December 01, .2014 and 15 ml on January 08, .2015. The activated carbon and all the apparatus setup was not changed during those experiments to have same initial conditions. The water temperature was also maintained so as it does not have any effect in the results. The data has been denoted by various alphabets for making it simpler to understand. For all of the samples,

T= Trial
R = Replicate
B = Before
A = After
Formula = TnRnA and TnRnB
n = number of samples = 1, 2, 3

5.2.1 Experimental setup

First, three identical buckets were taken and each were filled with 8l water and 5 ml of ‘X’ shampoo was added and thoroughly mixed. After that, the system was switched on and bypass mode was selected. The bypass was done for 1 minute and then the system was switched on to shower mode. Then, three samples were taken in a sampling bottle for measurement from the mixture before the process. Temperature of the water in the buckets were regularly monitored via temperature sensor. After that, all of the water was allowed to pass through the filter and again 3 samples were collected at the end of the process in a sampling bottle. The system was then switched to backwash mode for 1 minute and to bypass mode for 1 minute before the start of the next process. Similar repetitions were done for all of the buckets and for 10 ml and 15 ml concentrations. The below flow diagram helps better to understand the procedure.



5.3 Considerations

A number of elements were kept as constant as possible so as to not have any effect in the measurements.

5.3.1 Temperature

The temperature of the incoming sample water was kept at ~40 degrees. Also, all the measurements were performed in the laboratory and were in room temperature ~25 degrees.

5.3.2 Measurement errors

Measurement errors while measuring the amount of shampoo and measure of the tap water (8l) has also been not taken into account during the analysis of the chemical constituents.

5.3.3 Shower loop process

The shower loop elements like the activated carbon and the sand were not changed during the whole experiment while the UV ray was not used entirely.

5.3.4 Interval time

The interval time between each batches was ~2 minutes during which tap water was ran through the shower loop process with shower mode OFF i.e. in by pass mode. Also after each batch, a back wash was done for 1 minute.

6 Results

6.1 PH

The pH of all of the samples was measured at a laboratory temperature of 25 °C. Results are shown in the Table 12 and Figure 16.

Table 12. pH of the samples at 25 degree Celsius

Samples	Concentration	pH	Concentration	pH	Concentration	pH
T1R1B	5	5.9	10	7.38	15	7.34
T1R1A	5	8.44	10	7.41	15	7.47
T1R2B	5	6.17	10	7.31	15	7.47
T1R2A	5	8.96	10	7.39	15	7.46
T1R3B	5	6.63	10	7.31	15	7.36
T1R3A	5	8.81	10	7.35	15	7.59
T2R1B	5	6.58	10	7.30	15	7.62
T2R1A	5	9.03	10	7.35	15	7.51
T2R2B	5	6.57	10	7.30	15	7.43
T2R2A	5	9.09	10	7.35	15	7.49
T2R3B	5	6.57	10	7.28	15	7.38
T2R3A	5	9.12	10	7.36	15	7.38
T3R1B	5	6.59	10	7.29	15	7.39
T3R1A	5	8.96	10	7.33	15	7.35
T3R2B	5	6.83	10	7.27	15	7.31
T3R2A	5	8.92	10	7.32	15	7.38
T3R3B	5	6.81	10	7.26	15	7.24
T3R3A	5	8.92	10	7.4	15	7.38

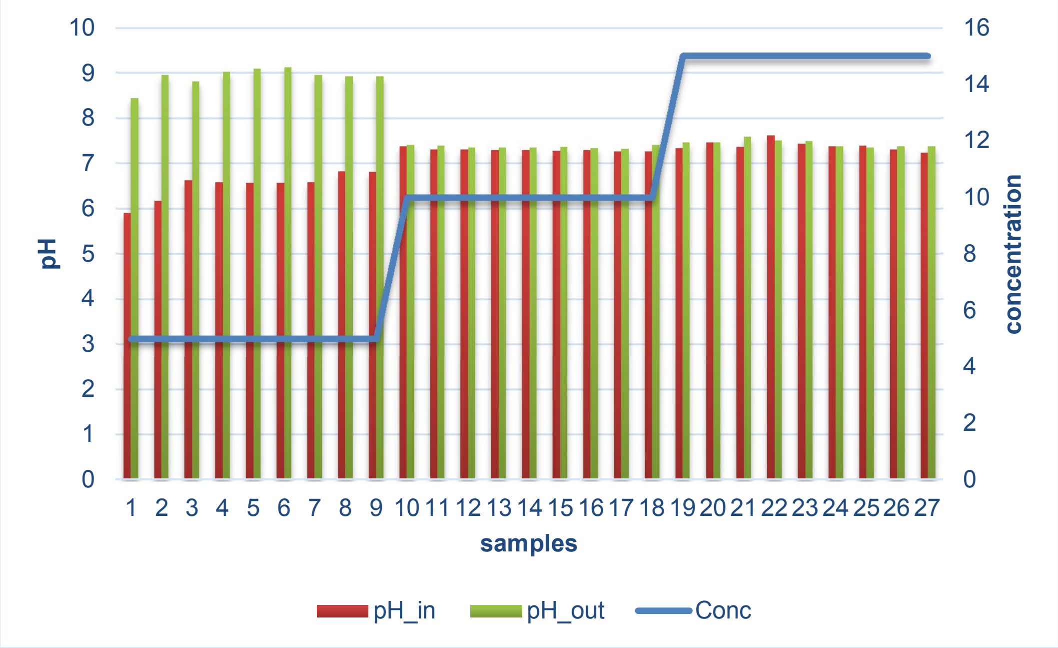


Figure 16. pH of the samples with different concentration

6.2 AES

The AES experiment was done to analyse potassium (K^+), magnesium (Mg^{++}) and calcium (Ca^{++}). Each of the element was analysed using different wavelengths and various set of experiments were performed for better analysis. Table 13 provides the amount of potassium before and after the process alongside the different concentration used, while Table 14 and 15 represents the data for calcium and magnesium respectively.

Table 13. Amount of Potassium before and after the process in the samples expressed in mg.

Samples	**Concentration**	**Potassium**	**Concentration**	**Potassium**	**Concentration**	**Potassium**
T1R1B	5	3.2	10	2.45	15	4.78
T1R1A	5	44.49	10	9.49	15	22.56
T1R2B	5	2.58	10	2.71	15	5.36
T1R2A	5	31.93	10	9.93	15	21.07
T1R3B	5	2.35	10	2.65	15	4.41
T1R3A	5	31.79	10	11.7	15	21.65
T2R1B	5	2.25	10	3.17	15	4.33
T2R1A	5	19.56	10	10.27	15	5.61
T2R2B	5	2.2	10	2.99	15	3.96
T2R2A	5	19.14	10	11.92	15	5.37
T2R3B	5	2.06	10	2.9	15	3.95
T2R3A	5	19.36	10	7.78	15	5.36

Samples	Concentration	Potassium	Concentration	Potassium	Concentration	Potassium
T3R1B	5	2.01	10	2.83	15	3.81
T3R1A	5	12.16	10	2.99	15	3.72
T3R2B	5	6.38	10	2.77	15	3.84
T3R2A	5	11.92	10	4.44	15	3.71
T3R3B	5	1.95	10	2.72	15	3.63
T3R3A	5	11.94	10	3.51	15	3.49

Table 14. Amount of Calcium before and after the process expressed in mg.

Samples	Concentration	Calcium	Concentration	Calcium	Concentration	Calcium
T1R1B	5	33.3	10	37.02	15	43.81
T1R1A	5	9.99	10	21.55	15	49.84
T1R2B	5	33.5	10	37.14	15	43.48
T1R2A	5	10.11	10	21.96	15	47.06
T1R3B	5	33.1	10	36.47	15	44.45
T1R3A	5	10.04	10	20.78	15	49.69
T2R1B	5	33.81	10	36.7	15	44.89
T2R1A	5	15.06	10	21.41	15	35.22
T2R2B	5	33.94	10	36.44	15	45.5
T2R2A	5	14.95	10	26.68	15	35.06
T2R3B	5	33.95	10	37.38	15	45.77
T2R3A	5	15.44	10	22.77	15	34.97
T3R1B	5	33.88	10	37.24	15	46.02
T3R1A	5	18.45	10	28.28	15	30.75
T3R2B	5	34.01	10	28.63	15	46.13
T3R2A	5	18.55	10	28.16	15	31.88
T3R3B	5	35.02	10	38.51	15	46.12
T3R3A	5	18.86	10	31.01	15	31.97

Table 15. Amount of Magnesium before and after the process expressed in mg.

Samples	Concentration	Magnesium	Concentration	Magnesium	Concentration	Magnesium
T1R1B	5	2.17	10	2.47	15	3.19
T1R1A	5	2.04	10	3.61	15	8.42
T1R2B	5	2.15	10	2.47	15	3.2
T1R2A	5	2	10	3.58	15	8.75
T1R3B	5	2.13	10	2.46	15	3.21
T1R3A	5	2.05	10	3.65	15	8.98
T2R1B	5	2.2	10	2.48	15	3.21
T2R1A	5	2.68	10	3.59	15	3.97
T2R2B	5	2.23	10	2.5	15	3.23
T2R2A	5	2.74	10	4.08	15	3.91

Samples	Concentration	Magnesium	Concentration	Magnesium	Concentration	Magnesium
T2R3B	5	2.26	10	2.49	15	3.21
T2R3A	5	2.82	10	3.58	15	3.98
T3R1B	5	2.25	10	2.51	15	3.24
T3R1A	5	3.2	10	2.17	15	3.24
T3R2B	5	2.28	10	2.52	15	3.18
T3R2A	5	3.25	10	2.51	15	3.35
T3R3B	5	2.3	10	2.5	15	3.23
T3R3A	5	3.24	10	2.51	15	3.46

6.3 Conductance

The conductance was measured with a conductivity meter (Metter Toledo). Table 16 and Figure 17 shows the amount of conductivity of the sample before and after the process. It can also be seen that the conductivity level decreases as the concentration increased except in Concentration 5, Batch 1 and Concentration 15, Batch 1 (Figure 17), where it increased.

Table 16. Measurement of Conductivity before and after the process expressed in Micro Siemens per cm.

Samples	Concentration	Conductivity (µs/cm)	Concentration	Conductivity (µs/cm)	Concentration	Conductivity (µs/cm)
T1R1B	5	185.4	10	220	15	248
T1R1A	5	246	10	190.7	15	299
T1R2B	5	184.9	10	225	15	249
T1R2A	5	207	10	189.4	15	292
T1R3B	5	187.4	10	219	15	250
T1R3A	5	205	10	190.4	15	297
T2R1B	5	192.2	10	220	15	253
T2R1A	5	178	10	167.7	15	172.6
T2R2B	5	195.2	10	219	15	252
T2R2A	5	179.4	10	163.7	15	175.5
T2R3B	5	195.4	10	227	15	252
T2R3A	5	181.2	10	164.2	15	172.3
T3R1B	5	194.8	10	229	15	249
T3R1A	5	164.1	10	168.1	15	163.6
T3R2B	5	194	10	232	15	250
T3R2A	5	164.5	10	164.5	15	159.2
T3R3B	5	208	10	229	15	251
T3R3A	5	166.4	10	165.7	15	156.5

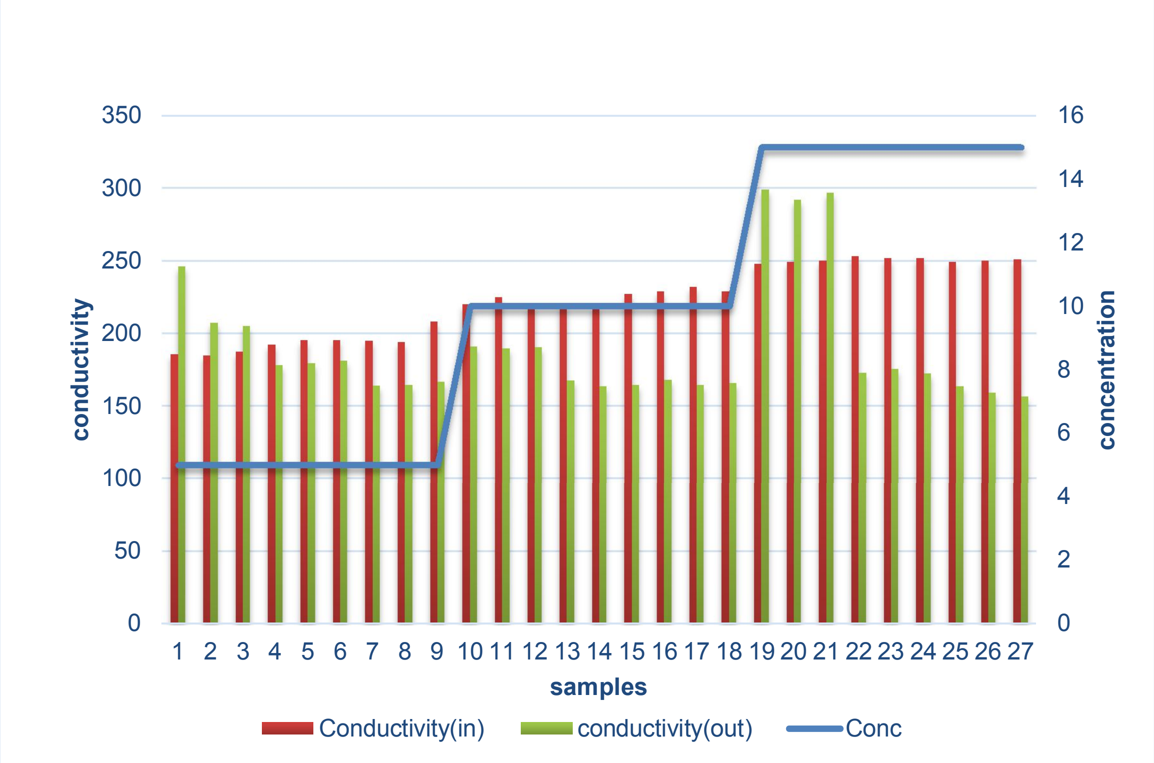


Figure 17. Conductivity of the samples with different concentration

6.4 Surface tension

The surface tension was measured with the DuNuoy measurement system. Table 13 represents the measurement values in mN/m for the samples before and after the process.

Table 17. Measurement of Surface Tension before and after the process expressed in mN /m.

Samples	Concentration	Surface_tension (mN/m)	Concentration	Surface_tension (mN/m)	Concentration	Surface_tension (mN/m)
T1R1B	5	29.8	10	29.8	15	28.1
T1R1A	5	71.3	10	66.1	15	65.3
T1R2B	5	31.3	10	29.7	15	28.1
T1R2A	5	71.6	10	71.2	15	70.6
T1R3B	5	32.9	10	29.9	15	28.4
T1R3A	5	72.3	10	69.7	15	70.9
T2R1B	5	30.9	10	29.8	15	27.8
T2R1A	5	72	10	71.8	15	71.8
T2R2B	5	31	10	30.5	15	27.9
T2R2A	5	71.6	10	56.8	15	71.9
T2R3B	5	31.5	10	30.1	15	27.8
T2R3A	5	72	10	72	15	71.8
T3R1B	5	31	10	31.5	15	27.9

Samples	Concentration	Surface_tension (mN/m)	Concentration	Surface_tension (mN/m)	Concentration	Surface_tension (mN/m)
T3R1A	5	70.9	10	71.6	15	69.7
T3R2B	5	29	10	29.6	15	28.2
T3R2A	5	72.3	10	70.8	15	66.3
T3R3B	5	31.2	10	29.8	15	28.3
T3R3A	5	72.7	10	71.8	15	69.4

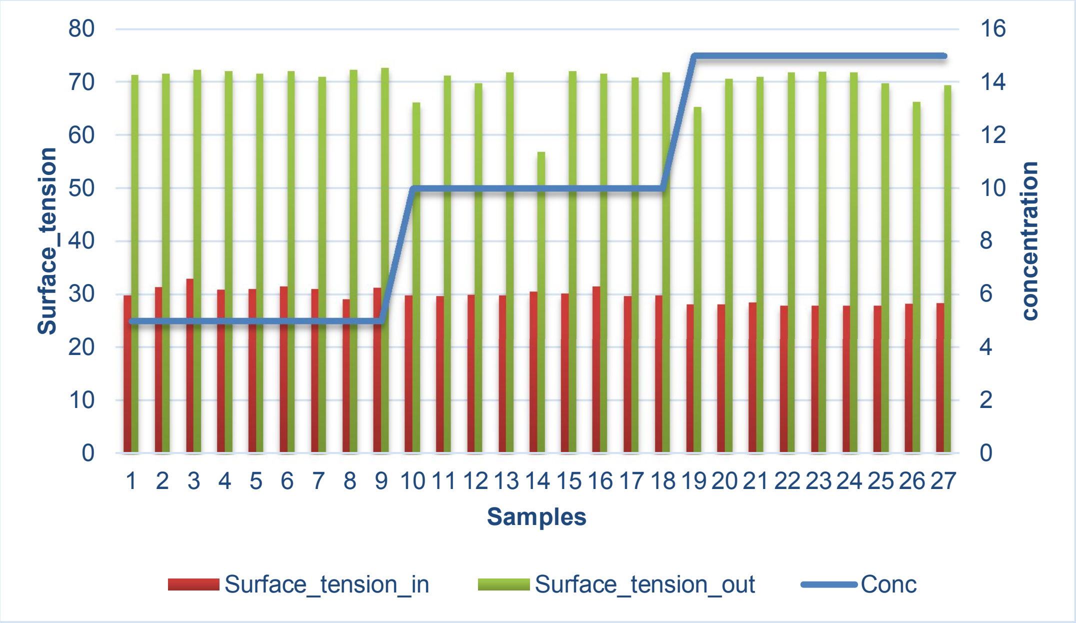


Figure 18. Surface tension of the samples with different concentration

6.5 Turbidity

The turbidity levels for the treated water were seen less than 1NTU with the exception of one experimental error. The maximum turbidity level for untreated water was found to be 229 NTU (Table 18). The turbidity levels before the process increase with the increase in concentration. However, after the process, the turbidity level is almost zero. (Figure. 19 and Table 18).

Table 18. Measurement of Turbidity before and after the process expressed in NTU.

Samples	Concentration	Turbidity	Concentration	Turbidity	Concentration	Turbidity
T1R1B	5	40.5	10	114	15	207
T1R1A	5	0.56	10	0.2	15	0.55
T1R2B	5	39.1	10	113	15	187
T1R2A	5	1.21	10	0.43	15	0.51
T1R3B	5	38.7	10	124	15	211
T1R3A	5	0.58	10	0.42	15	0.38

Samples	Concentration	Tur-bidity	Concentration	Tur-bidity	Concentration	Tur-bidity
T2R1B	5	54.5	10	104	15	210
T2R1A	5	0.43	10	0.22	15	0.6
T2R2B	5	63.4	10	117	15	206
T2R2A	5	0.34	10	19.5	15	0.74
T2R3B	5	59.4	10	105	15	210
T2R3A	5	0.42	10	0.5	15	0.29
T3R1B	5	45.9	10	134	15	210
T3R1A	5	0.38	10	0.39	15	0.44
T3R2B	5	50.1	10	132	15	229
T3R2A	5	0.71	10	0.32	15	0.25
T3R3B	5	42.8	10	140	15	184
T3R3A	5	0.69	10	0.33	15	0.24

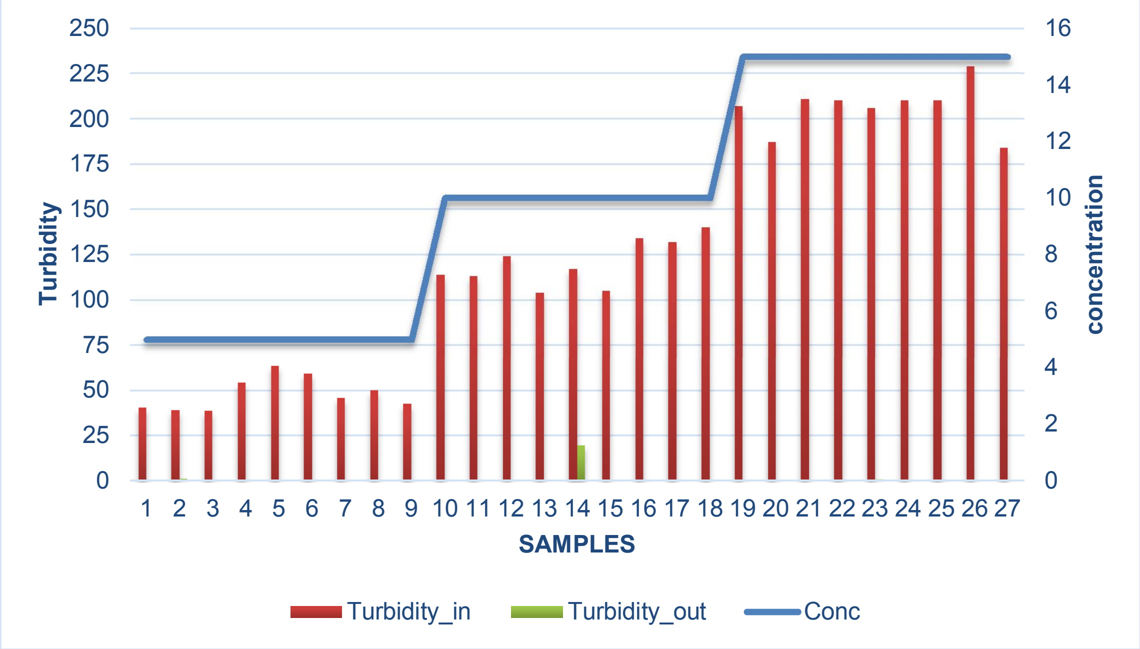


Figure 19. Turbidity levels for samples with different concentrations represented in NTU

6.6 Ion chromatography

Ion chromatography was measured by metrohm IC 761, and it was used to measure fluoride (Table 19), Chloride (Table 20), Sulphate (Table 21) and Phosphate (Table 22).

Table 19. Measurement of fluoride before and after the process expressed in mg.

Samples	Concentration	Fluoride (mg)	Concentration	Fluoride (mg)	Concentration	Fluoride (mg)
T1R1B	5	0.507	10	0.497	15	0.37
T1R1A	5	0.42	10	0.282	15	0.157
T1R2B	5	0.425	10	0.271	15	0.248
T1R2A	5	0.152	10	0.221	15	0.103
T1R3B	5	0.328	10	0.291	15	0.34
T1R3A	5	0.191	10	0.175	15	0.133
T2R1B	5	0.47	10	0.276	15	0.306
T2R1A	5	0.134	10	0.168	15	0.131
T2R2B	5	0.471	10	0.265	15	0.303
T2R2A	5	0.18	10	0.258	15	0.167
T2R3B	5	0.452	10	0.402	15	0.296
T2R3A	5	0.171	10	0.233	15	0.171
T3R1B	5	0.436	10	0.244	15	0.278
T3R1A	5	0.263	10	0.174	15	0.133
T3R2B	5	0.448	10	0.26	15	0.286
T3R2A	5	0.207	10	0.27	15	0.159
T3R3B	5	0.457	10	0.642	15	0.281
T3R3A	5	0.171	10	0.083	15	0.113

Table 20. Measurement of chloride before and after the process expressed in mg.

Samples	Concentration	Chloride (mg)	Concentration	Chloride (mg)	Concentration	Chloride (mg)
T1R1B	5	10.886	10	20.937	15	33.151
T1R1A	5	12.583	10	10.591	15	5.963
T1R2B	5	9.568	10	19.307	15	25.166
T1R2A	5	4.497	10	11.325	15	7.955
T1R3B	5	13.757	10	21.332	15	24.649
T1R3A	5	5.223	10	12.513	15	6.852
T2R1B	5	14.218	10	21.621	15	25.634
T2R1A	5	4.85	10	10.272	15	8.5578
T2R2B	5	10.18	10	20.331	15	25.942
T2R2A	5	4.729	10	14.251	15	8.018
T2R3B	5	10.304	10	11.847	15	25.626
T2R3A	5	4.933	10	7.3	15	6.732
T3R1B	5	9.415	10	14.896	15	25.545
T3R1A	5	4.539	10	5.541	15	10.391
T3R2B	5	10.197	10	20.137	15	25.778
T3R2A	5	4.592	10	8.219	15	10.094
T3R3B	5	12.439	10	22.453	15	25.353
T3R3A	5	4.444	10	5.437	15	9.088

Table 21. Measurement of phosphate before and after the process expressed in mg.

Samples	Concentration	Phosphates (mg)	Concentration	Phosphates (mg)	Concentration	Phosphates (mg)
T1R1B	5		10		15	
T1R1A	5	2.187	10	0.277	15	0.234
T1R2B	5		10		15	
T1R2A	5	2.49	10	0.336	15	0.221
T1R3B	5		10		15	
T1R3A	5	2.931	10	0.336	15	0.352
T2R1B	5		10		15	
T2R1A	5	0.982	10	0.264	15	0.493
T2R2B	5		10		15	
T2R2A	5	1.052	10	0.223	15	0.46
T2R3B	5		10		15	
T2R3A	5	1.052	10	0.239	15	0.362
T3R1B	5		10		15	
T3R1A	5	0.47	10	0.24	15	0.27
T3R2B	5		10		15	
T3R2A	5	0.523	10	0.086	15	0.201
T3R3B	5		10		15	
T3R3A	5	0.552	10	0.7	15	0.332

Table 22. Measurement of sulphate before and after the process expressed in mg.

Samples	Concentration	Sulphates (mg)	Concentration	Sulphates (mg)	Concentration	Sulphates (mg)
T1R1B	5	13.051	10	15.532	15	17.163
T1R1A	5	10.322	10	12.463	15	10.456
T1R2B	5	12.05	10	14.497	15	17.031
T1R2A	5	11.372	10	13.414	15	13.036
T1R3B	5	16.207	10	16.243	15	16.71
T1R3A	5	13.067	10	14.444	15	12.448
T2R1B	5	15.354	10	16.41	15	17.318
T2R1A	5	10.651	10	11.644	15	15.064
T2R2B	5	12.387	10	15.382	15	17.886
T2R2A	5	10.907	10	16.547	15	13.545
T2R3B	5	11.743	10	9.148	15	17.344
T2R3A	5	10.695	10	10.757	15	11.824
T3R1B	5	11.651	10	11.076	15	17.313
T3R1A	5	10.849	10	14.849	15	16.46
T3R2B	5	11.952	10	14.258	15	17.808
T3R2A	5	10.84	10	16.92	15	16.177
T3R3B	5	12.167	10	15.939	15	17.383
T3R3A	5	10.762	10	13.157	15	15.626

7 Analysis of water quality parameters

7.1 Turbidity

For recycled shower water, the turbidity specified criteria are as follows; 1 NTU is desirable, but the permissible amount is 5 NTU. In this thesis, 98.8 % of the cycles, the desirable standard of less than 1 NTU was achieved (Table 18 and Figure 19). Only once, it exceeded 5 NTU (T2R2A), possibly of due to an experimental error.

7.2 pH

The recycled shower water had its pH levels increased slightly for the shampoo concentration of 5 ml while the pH remained almost the same before and after the process (Table 8, Figure 16), as the normal pH of water lies in between 6.5 -9.5, the data shows that the pH of the processed water lies in that range. The reason for the slight increase was due to the higher operating temperatures for the first Concentration level.

7.3 Hardness

The hardness of water is indicated by the levels of calcium and magnesium (Table 13, 14). The calcium levels decreased significantly whereas there was a slight increase in the potassium levels (Figure 21). Water is considered hard when the total amount of Ca and Mg crosses more than 180 mg/l (USGS). However, this level was not exceeded during the whole experiment.

7.4 Conductivity

The conductivity level generally decreased after the process with two exceptions in Concentration 5 Batch 1 and Concentration 15 Batch 1 (Table 16, Figure 17). The reason behind that could be the lack of backwash, and the increase in the potassium level and also since the fact that the samples were the first measurements of the day, and the system was not used continuously, the pre-existing conditions like the temperature and the could have affected the process ability.

8 Analysis of other elements

8.1 Ion Chromatography

The difference between before and after the process can be seen in Figure 20 for fluoride, chloride, phosphate and sulphate. The Figure shows that the largest decrease is seen in the case of chloride, and the second compound to decrease was sulphate. However, there seems to be very small difference in the amounts of fluoride and phosphate. The fact that all the elements either decreased or had a slight effect proves that the process is working well.

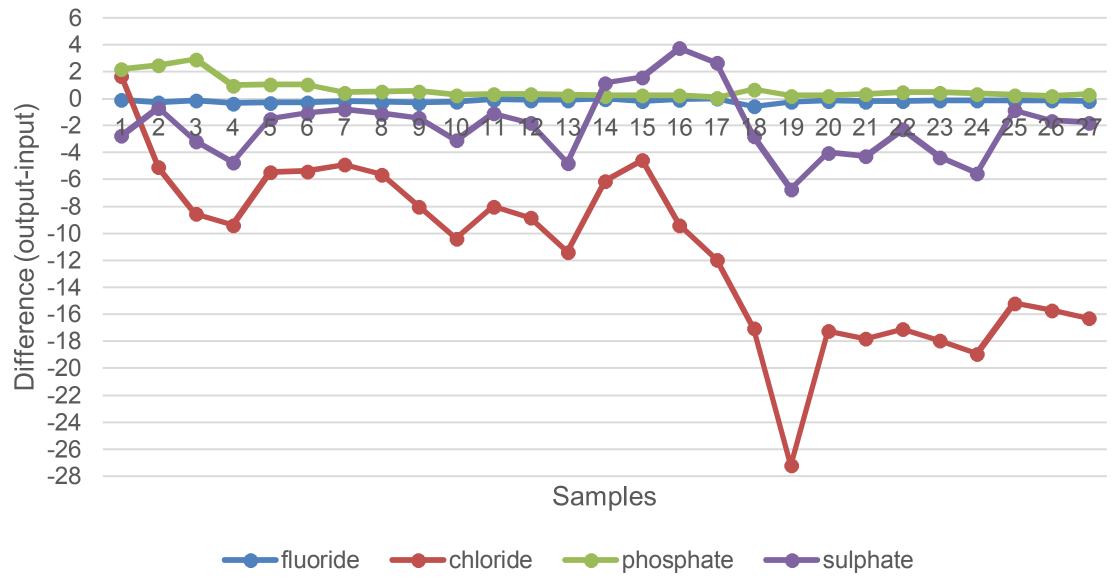


Figure 20. Difference in the amount of F^-, Cl^-, $PO_4{}^{3-}$ and $SO_4{}^{2-}$ before and after the process

8.2 AES

Figure 21 shows the difference between the amount of calcium, magnesium and potassium levels before and after the process. The figure illustrates the decrease in the levels of calcium while the level of magnesium remains almost unchanged through the experiment. The largest fluctuations can be seen in the amount of potassium which gradually decreases as the level of concentration rises. Also, the levels of potassium magnesium and calcium seems to have same pattern of change when the concentration rises. Since the shower loop was not used for many days and lack of backwash along with bypass seem to have increased the levels of all elements for samples 19, 20 and 21 (Concentration 15, Batches 1).

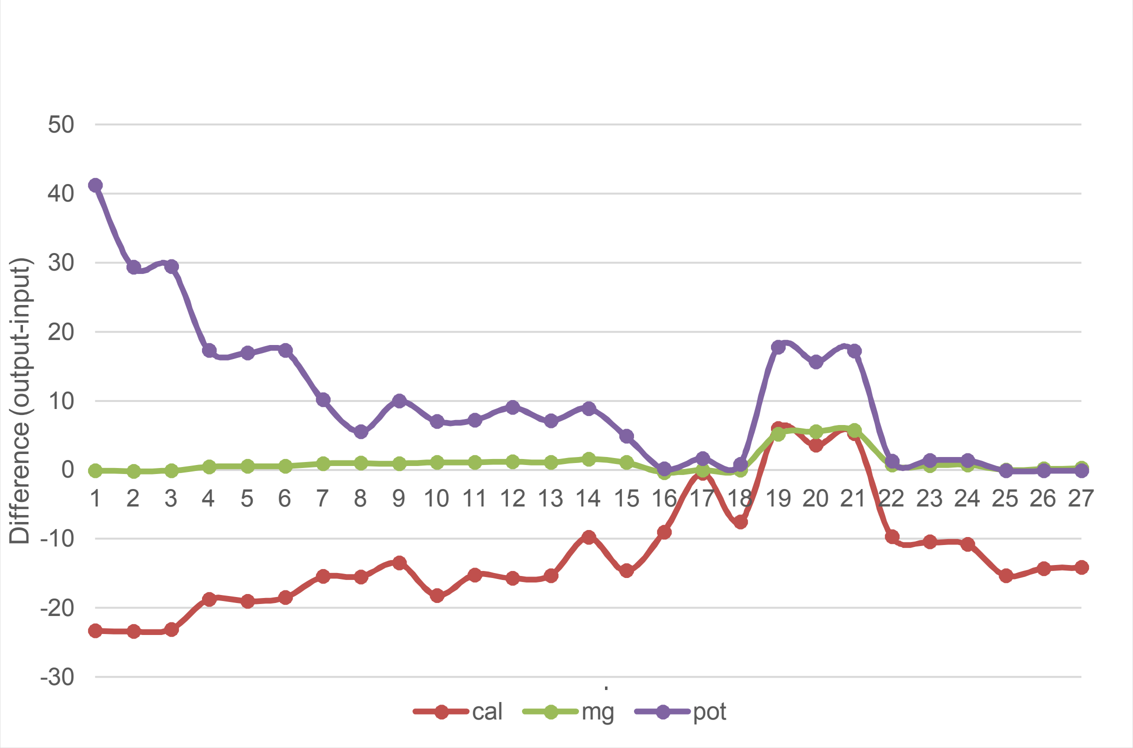


Figure 21. Difference of the amount of Ca, Mg and K between before and after the process

9 Statistical analysis by ANOVA

ANOVA (Analysis of Variance) is a mathematical process for separating the variability of a group of observations into assignable tests. (Itl.nist.gov, 2015). It provides a statistical test concerning if the means of these several groups are all equal. The analysis of variance were first developed by R.A. Fischer in the 1920s and 1930s. (Wu. Xiao, 2009)

The *p* value column gives the probability value of each coefficient and on the right of p value column are the stars that show the level of significance of the coefficients. Highly significant coefficients are denoted by three stars and their *p* value is almost zero. (Dulal, Bipin, 2014). Statistical significance decreases with the decrease in number of stars but two stars and one star are still mathematically significant and are included in the model. The dot symbol '.' and empty ' ' shows that the coefficients are not significant and are ignored in the model.

Anova was done by using GAD or Analysis of Variance from General Principles, which analyses complex ANOVA models with any combination of orthogonal /nested and fixed/random factors. The restrictions for using GAD are (i) data must be balanced and (ii) fixed nested factors are not allowed. In our case, the fixed factor is concentration and the random variable are batches.

9.1 Cochran's test

C test is a Cochran's test of the null hypothesis that the largest variance in several samples variances are the same. For the data, a C test was performed and analysed, some of the examples can be seen in the Appendix 6. (cran.r.project.org, 2015). The null and alternate hypothesis for C test are:

H0: All variances are equal.

Ha: At least one variance value is significantly larger than the other variance values.

9.2 Box plots

A box plot is a graphical rendition of statistical data based on the minimum, first quartile median, third quartile and maximum. The term "box plot" comes from the fact that graph looking like a rectangle with lines extending from the top and bottom thus sometimes called box and whisker plot. In a typical box plot (Figure 22), the top of the rectangle indicates the third quartile, a horizontal line near the middle of the rectangle indicates the median, and the bottom of the rectangle indicates the first quartile. (Berthouex, Brown, 2002). A vertical line extends from the top of the rectangle to indicate the upper whisker end or maximum value, and another vertical line extends from the bottom of the rectangle to indicate the lower whisker end or minimum value. The figure also shows the example with the median, first quartile and the third quartile. (Whatis.com, 2015). Outliers as in case of box plots are not usually well defined in statistics and the definition varies according to purpose and situation. In box plot, outliers are identified as any points that are more than 1.5 IQRs above Q3 or 1.5 IQRs below Q1. (Seltman, J, 2014)

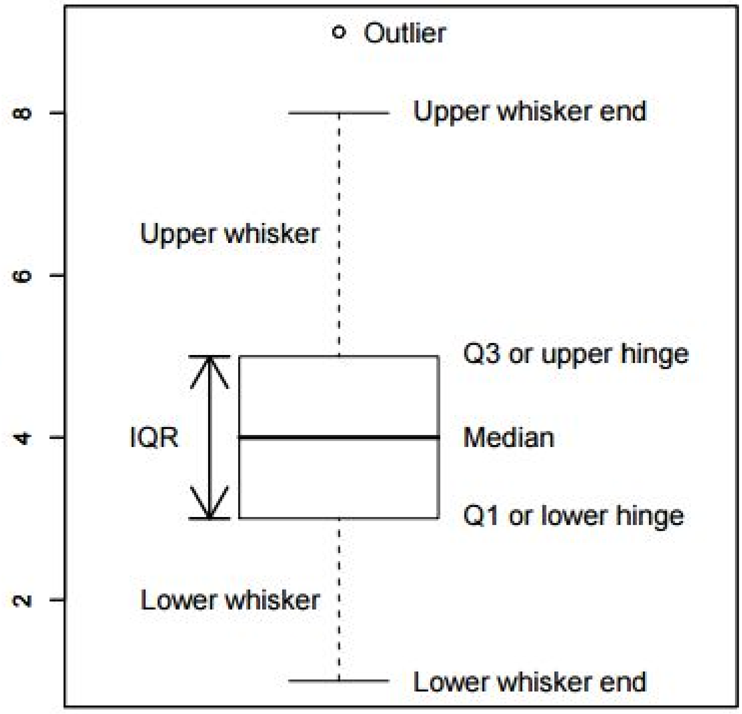


Figure 22. An annotated box plot (Seltmann, J, 2014)

9.3 Hypotheses

Statistical analysis using two way anova was done in R studio to see the whether concentration or batches in concentration had a major effect on the process. First, concentration was regarded as fixed variable while batches were considered as random variable. A GAD package was installed in R studio and their variance was analysed. To find out, analysis of the variance table for the difference was created for all of the responses. After that, a summary table (Table 23) was created to see if the concentration or the interaction had any significant effect in the measurement. Box plots were created for the difference to see the effect of concentration in different batches. The hypotheses tested were as follows:

Ho: There is no significant effect of concentration in the amount of measured elements before and after the process.
H1: There is a significant effect between concentration and the amount of measured elements before and after the process.

Table 23. Dependency of the different elements to the concentration and the batches with the difference of values before and after the process according to the P values.

Concentration Dependent	**Batches : Concentration Interaction Dependent**	**Concentration and Interaction Independent**
Cl**	Ca***	St
	Mg***	F
	K***	SO4
pH***	pH*	
T***	T**	
	CO***	
	PO4***	

Signif. codes: 0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

*** = Highly significant

* and ** = Significant

Table 23 provides the overall dependency of different elements on the concentration and to which the null hypothesis can be rejected or accepted. Since, for surface tension, fluoride and sulphate, the null hypothesis is accepted which suggests that there is no significant effect of concentration and batches on the measured elements before and after the process. However, the rest of the other elements depend more on concentration or in the interaction. Chlorine, is dependent only on the concentration, while, for pH and turbidity, concentration has highly significant effect; however, batches have significant effect on both of them. Calcium, magnesium, potassium, conductivity and phosphate are significantly affected by the batches, but the concentration has no effect on the difference. The details of the anova can be found in Appendix 4. Since, 3 types of effect was seen in the case of the data, analyses using anova and box plot were done.

9.3.1 Case I: Concentration dependent

Chlorine was taken as an example for this analysis and similar results can be seen for pH and turbidity.

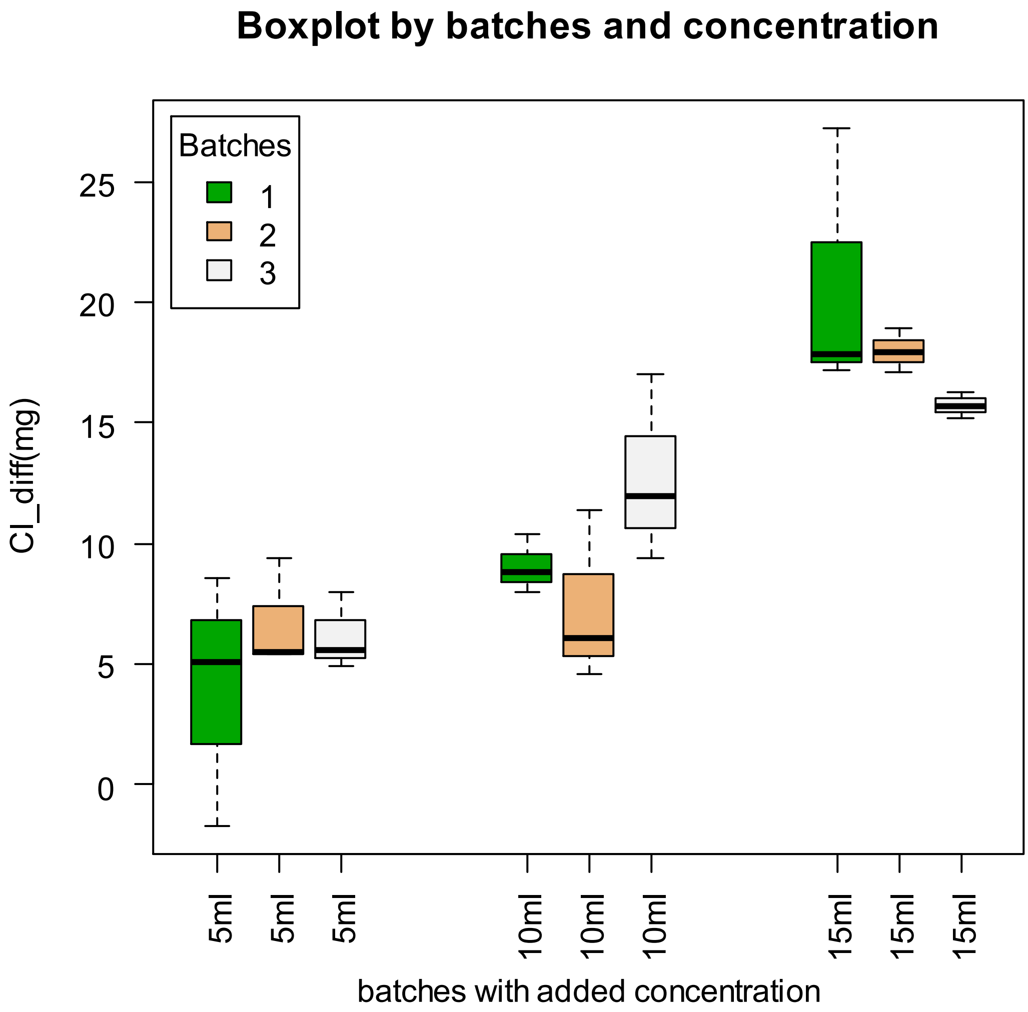
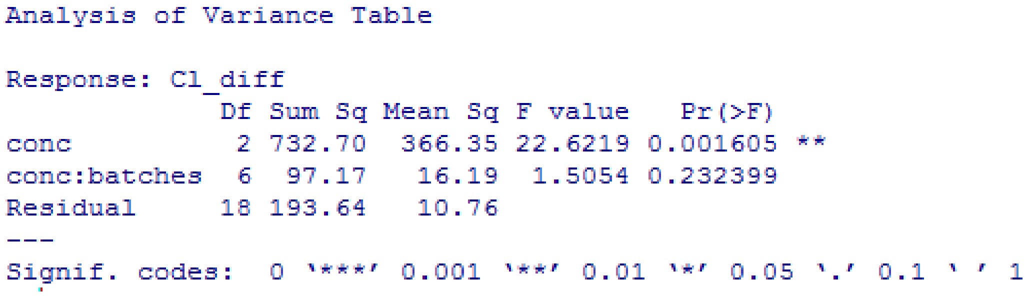


Figure 23. Box plots of different batches (1,2,3) for chlorine according to their concentrations (5, 10, 15)



```
Analysis of Variance Table

Response: Cl_diff
             Df Sum Sq Mean Sq F value   Pr(>F)
conc          2 732.70  366.35 22.6219 0.001605 **
conc:batches  6  97.17   16.19  1.5054 0.232399
Residual     18 193.64   10.76
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Figure 24 Analysis of the variance table for chlorine difference between before and after

Figure 23 illustrates the box plots for the difference in chlorine as mg before and after the process. All the box plots shows that the amount of chlorine is decreasing except for Concentration 5 ml Batch 1 and except Batch 2 in 5 ml of Concentration and Batch 1 of 15 ml. The median line can be seen increasing as the concentration rises These results are backed by the anova tables (Figure 24) which shows that there is a significant effect of concentration on the difference level thus rejecting the null hypothesis and accepting the alternative hypothesis for concentration whereas the batches concentration interaction are not significant as in some cases, the level rises while in other cases, they decrease. Further investigation via C test reveals that concentration 15 ml first batch has outlying variance, (Appendix 6, figure. 31), and the Student Newman Keuls (snk) test was done to check which of the concentration had the most significant effect, which revealed that the first concentration was the most significant, followed by 10 ml and 15 ml concentrations. . (Appendix 7, figure 34)

9.3.2 Case II: Batches: Concentration Interaction dependent

Case II can be seen in case of many measured elements like Ca, Mg, K, pH, turbidity, conductivity and PO_4. Except for pH and turbidity, the rest of the elements are highly significantly affected by the batches in concentration and not by the concentration levels. One of such example $PO_{4,}$ is studied in further detail with the box plots and anova table, while others have similar trends.

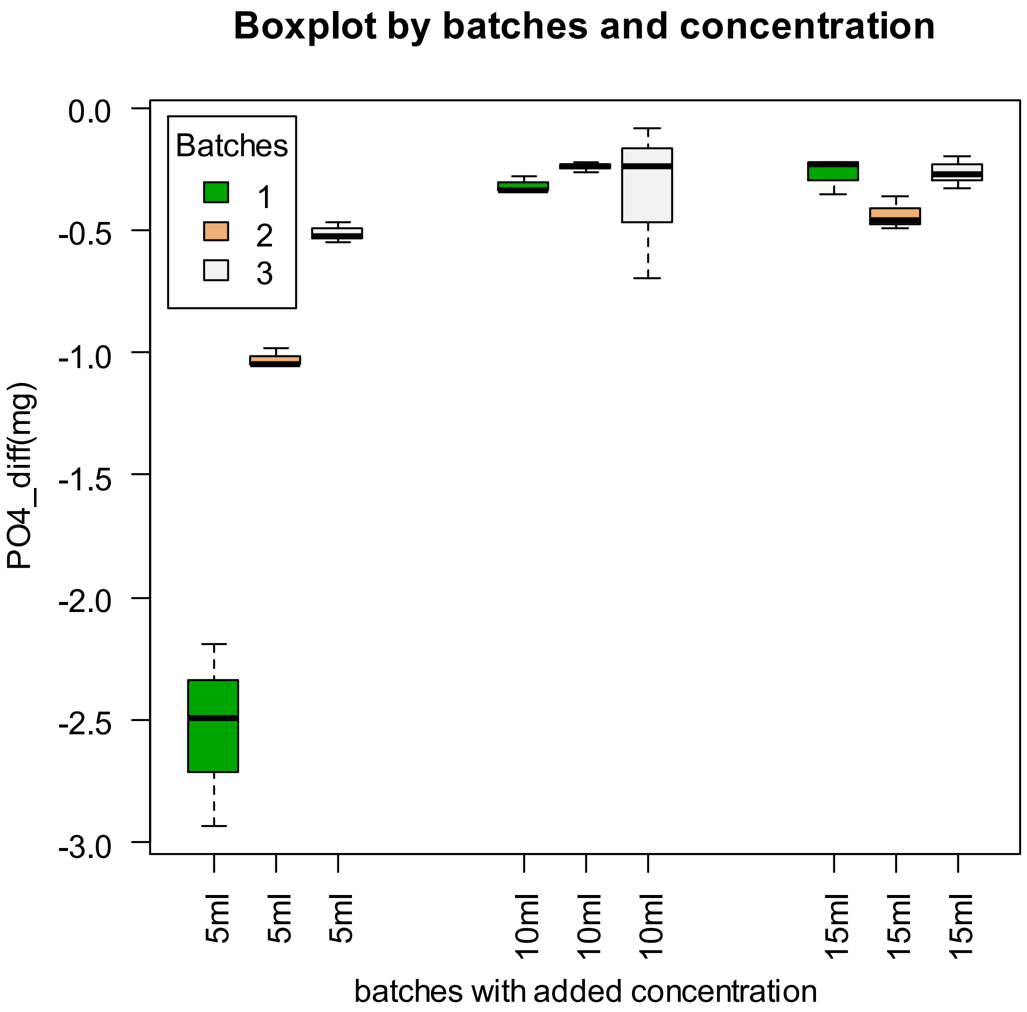
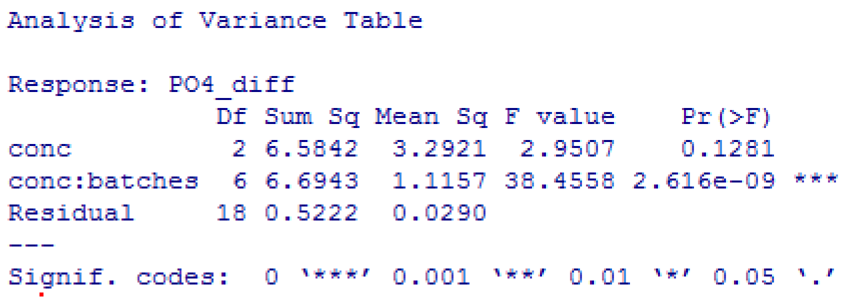


Figure 25. Box plots of different batches (1,2,3) for phosphate according to their concentrations (5, 10, 15)



```
Analysis of Variance Table

Response: PO4_diff
             Df Sum Sq Mean Sq F value    Pr(>F)
conc          2 6.5842  3.2921  2.9507    0.1281
conc:batches  6 6.6943  1.1157 38.4558 2.616e-09 ***
Residual     18 0.5222  0.0290
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Figure 26. Analysis of the variance table for phosphate difference between before and after the process

Box plots in Figure 25 show that the level of phosphate is increasing in all of the concentrations with larger effect seen in case of the first batch of 5ml. The median line does not increase from the first concentration to the second one while there is no significant change from 10 ml to 15 ml. In contrast, the difference is more significant to the interaction of batches and concentration. This results can also be seen with the help of anova table (Figure 26), which shows that the interaction is highly significant thus rejecting the null hypothesis. However, for concentration, the null hypothesis is accepted which states that there is no significant effect of concentration in the amount of measured elements before and after the process. The C test (Appendix 6, Figure. 32) reveals that the first batch of 5 ml has an outlying variance. The snk test was performed so as to see which or all of the interaction was significant. The results shows (Appendix 7, Figure 35), that not all of the level was significant but only concentration 5 ml was significant.

9.3.3 Case III: Concentration and Interaction independent

Case III represents those elements that are not dependent on the concentration and interaction. Similar trends can be seen with the elements like surface tension and fluoride.

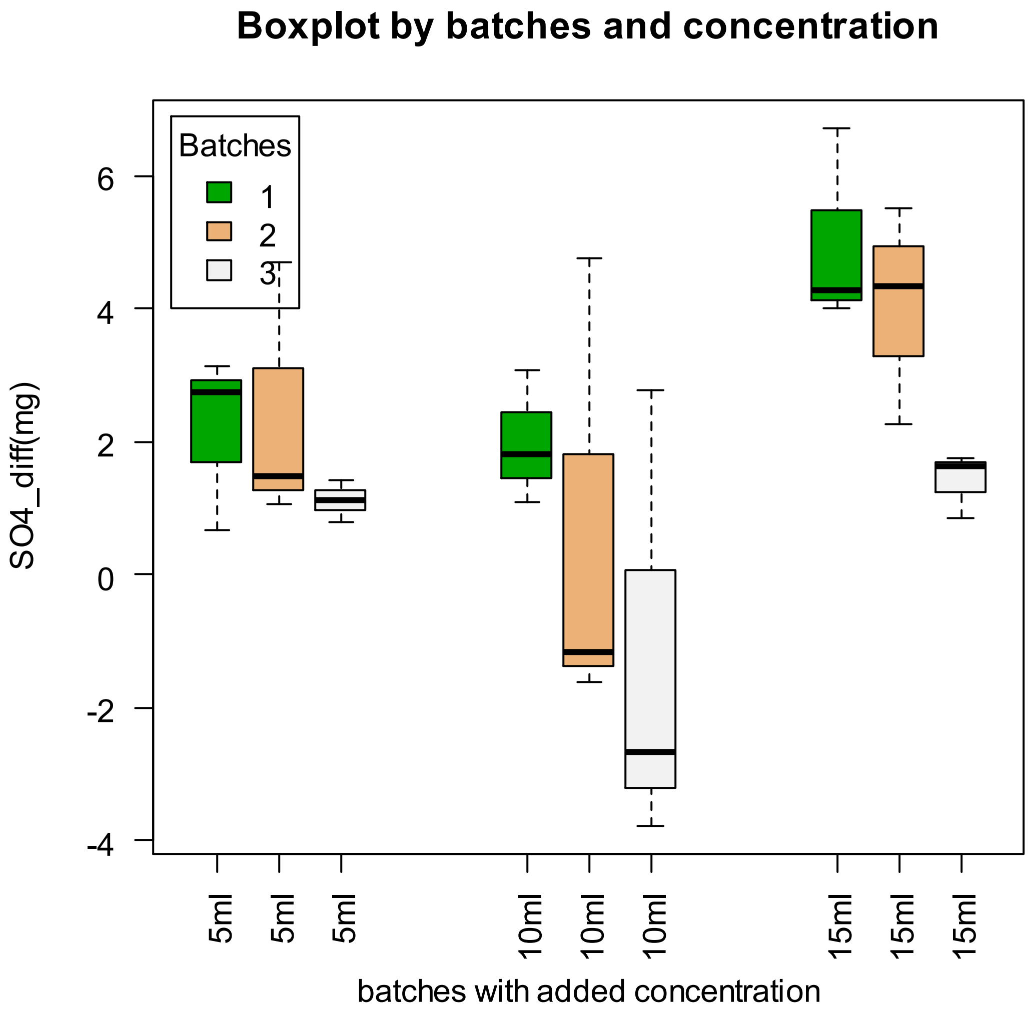
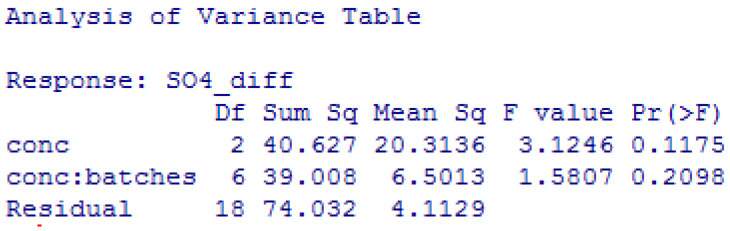


Figure 27. Box plots of different batches (1,2,3) for sulphate according to their concentrations (5, 10, 15)



```
Analysis of Variance Table

Response: SO4_diff
             Df Sum Sq Mean Sq F value Pr(>F)
conc          2 40.627 20.3136  3.1246 0.1175
conc:batches  6 39.008  6.5013  1.5807 0.2098
Residual     18 74.032  4.1129
```

Figure 28. Analysis of the variance table for sulphate difference between before and after the process

Figure 27 shows the box plots for sulphate with different batches and with different concentrations of shampoo. The median line as seen from the figure does not change significantly with the increasing concentration. Within the batches, the median decreases with the each set of experiments suggesting the increase of sulphate levels. Figure 28 shows the anova table which indicates the *p* value is greater than 0.05 concentration, thus accepting the null hypothesis, while the interaction of batches and concentration is also not significant. The C test of homogeneity of variances (Appendix 6, Figure.33) shows that the concentration 10 ml batch 2 has outlying variance. The snk test (Appendix 7, Figure 36) shows that there are no significant with the pairwise interaction among levels of batches within the concentration.

10 Removal efficiencies

The removal efficiencies for all of the compounds were calculated and can be seen in table 20. The negative (-) sign represents the increment from the input or from before the process while the positive sign is for removal percentage. The target of the process was to decrease all the amount varies except for that of surface tension which needs to increase in order for the system to be working properly. The highest average removal percentage was observed for turbidity (98.8 %) followed by chloride removal (55.89 %), fluoride (46.28 %), calcium removal (34.06 %). The average conductivity and sulphate removal were 13.6 % and 11.6 % respectively. The other elements had their amount increased, the highest increment was seen in case of potassium (370.09%), surface tension (136 94 %), phosphate (66.17 %). Magnesium and pH increased by 39.05 and 12.86 %, respectively. The table illustrates the process is more efficient as the concentration of the shampoo rises

Table 24. Removal efficiencies for each of the measured elements for all the samples expressed in percentage

Conc	calcium	magnesium	potassium	PH	surface_tension	turbidity	conductivity	fluoride	chloride	phosphate	sulphate
5.00	70.00	5.99	1290.31	43.05	139.26	98.62	-32.69	17.16	-15.59	-218.70	20.91
5.00	69.82	6.98	-1137.60	-45.22	-128.75	96.91	-11.95	64.24	53.00	-249.00	5.63
5.00	69.67	3.76	-1252.77	-32.88	-119.76	98.50	-9.39	41.77	62.03	-293.10	19.37
5.00	55.46	-21.82	-769.33	-37.23	-133.01	99.21	7.39	71.49	65.89	-98.20	30.63
5.00	55.95	-22.87	-770.00	-38.36	-130.97	99.46	8.09	61.78	53.55	-105.20	11.95

Conc	**calcium**	**magnesium**	**potassium**	**PH**	**surface_tension**	**turbidity**	**conductivity**	**fluoride**	**chloride**	**phosphate**	**sulphate**
5.00	54.52	-24.78	-839.81	-38.81	-128.57	99.29	7.27	62.17	52.13	-105.20	8.92
5.00	45.54	-42.22	-504.98	-35.96	-128.71	99.17	15.76	39.68	51.79	-47.00	6.88
5.00	45.46	-42.54	-86.83	-30.60	-149.31	98.58	15.21	53.79	54.97	-52.30	9.30
5.00	38.46	-40.87	-512.31	-30.98	-133.01	98.39	20.00	62.58	64.27	-55.20	11.55
10.00	49.05	-46.15	-287.35	-0.41	-121.81	99.82	13.32	43.26	49.41	-27.70	19.76
10.00	40.87	-44.94	-266.42	-1.09	-139.73	99.62	15.82	18.45	41.34	-33.60	7.47
10.00	43.02	-48.37	-341.51	-0.55	-133.11	99.66	13.06	39.86	41.34	-33.60	11.08
10.00	41.66	-44.76	-223.97	-0.68	-140.94	99.79	23.77	39.13	52.49	-26.40	29.04
10.00	26.78	-63.20	-298.66	-0.68	-86.23	83.33	25.25	2.64	29.91	-22.30	-7.57
10.00	39.09	-43.78	-168.28	-1.10	-139.20	99.52	27.67	42.04	38.38	-23.90	-17.59
10.00	24.06	13.55	-5.65	-0.55	-127.30	99.71	26.59	28.69	62.80	-24.00	-34.06
10.00	1.64	0.40	-60.29	-0.69	-139.19	99.76	29.09	-3.85	59.18	-8.60	-18.67
10.00	19.48	-0.40	-29.04	-1.93	-140.94	99.76	27.64	87.07	75.78	-70.00	17.45
15.00	-13.76	-163.95	-371.97	-1.77	-132.38	99.73	-20.56	57.57	82.01	-23.40	39.08
15.00	-8.23	-173.44	-293.10	0.13	-151.25	99.73	-17.27	58.47	68.39	-22.10	23.46
15.00	11.79	179.75	390.93	3.13	-149.65	99.82	-18.80	60.88	72.20	-35.20	25.51
15.00	21.54	-23.68	-29.56	1.44	-158.27	99.71	31.78	57.19	66.62	-49.30	13.02

Conc	**calcium**	**magnesium**	**potassium**	**PH**	**surface_tension**	**turbidity**	**conductivity**	**fluoride**	**chloride**	**phosphate**	**sulphate**
15.00	22.95	-21.05	-35.61	-0.81	-157.71	99.64	30.36	44.88	69.09	-46.00	24.27
15.00	23.60	-23.99	-35.70	0.00	-158.27	99.86	31.63	42.23	73.73	-36.20	31.83
15.00	33.18	0.00	2.36	0.54	-149.82	99.79	34.30	52.16	59.32	-27.00	4.93
15.00	30.89	-5.35	3.39	-0.96	-135.11	99.89	36.32	44.41	60.84	-20.10	9.16
15.00	30.68	-7.12	3.86	-1.93	-145.23	99.87	37.65	59.79	64.15	-33.20	10.11
AVERAGE	**34.06**	**-39.05**	**-370.09**	**-12.86**	**-136.94**	**98.78**	**13.60**	**46.28**	**55.89**	**-66.17**	**11.61**

10.1 Phosphates formation and increase in potassium levels

There was formation of phosphate compound (Table 21) and increase in potassium levels (Table 13,) which affected the removal efficiencies (Table 24) largely due to the activated carbon properties. Activated carbon does not adsorb the potassium and also adds small amount of phosphate depending on formation or manufacturing process. (Van Winkle, 2000). The amount is significant if the water is used as drinking water but since, this process is not used as a replacement of drinking water filtration, the values seems acceptable for potassium and within the range of shower water quality (Table 25). However, for phosphate levels some recommendations are to be made.

11 Comparisons

11.1 Comparison to the drinking water standards

The following data (Table 25) shows the comparison of the drinking water and the process water. The WHO guidelines and the European directives are studies to find out the difference between the processed water and the drinking water. The result concludes the findings of this experiment and suggests that except for phosphate levels, all of the measured contents were just within the range or exceeded it with a small amount (potassium).

Table 25. Data comparison of the process water and drinking water quality based on WHO guide lines and European guidelines. (Mäkinen, R, 2008, potassium in drinking water, 2015, Whqlibdoc.who.int, 2011)

Parameter	**Drinking water quality**	**Process water quality (Average)**	**Note**
pH	6.5-9.5	7.04	Within range
Mg (mg/l)	50	3.75	Not exceeded
K (mg/l)	8*	13.59	Exceeded with small amount
Ca (mg/l)	>20**	25.94	Within range
Conductivity	250	190.51	Not exceeded
Surface tension	71.97***	70.23	Not exceeded
Turbidity	5****	1.17	Not exceeded
Fluoride (mg/l)	1.5	0.19	Not exceeded
Chloride (mg/l)	250	7.76	Not exceeded
Phosphate (mg/l)	0.01-0.03	0.66******	Exceeded with large amount
Sulphate (mg/l)	<100	12.90	Not exceeded

* Treated tap water, the acceptable limit for 100 mg/l hard water is 82 mg/l

** Amount of calcium that has to be in drinking water, the threshold value is 200 mg/l.

*** The surface tension for pure water at 25 °C.

**** The highest turbidity level allowed for drinking water, the lowest or more desirable is less than 1 NTU.

******.The average value for phosphate for shower water quality is 1.63 mg/l

11.2 Comparison to previous tests

Similar turbidity tests done in 2013, before and after the process showed an average 99% removal while other elements were also removed. The samples were taken in the interval of 2 min and measurements were performed without the addition of shampoo. However, the initial concentration of test dust was 1 g/l 261 NTU for turbidity, 2.425 mg/l for ammonium hydroxide and 4 *10^6 CFU for bacteria. (Selvarajan, J, Holland, K, 2014)

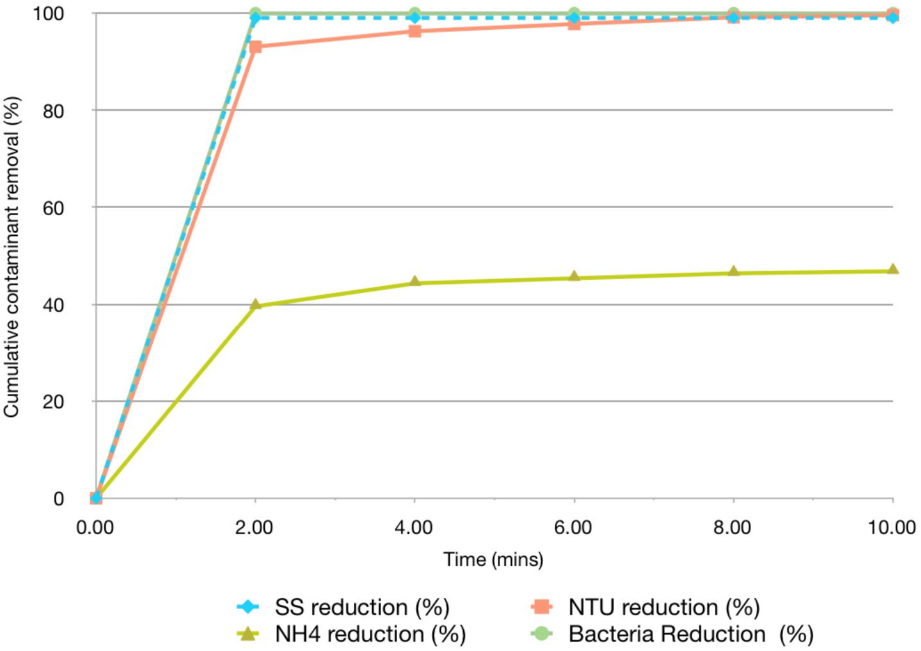


Figure 29. Cumulative contaminant removal over time in percentage. (Selvarajan, J, Holland K, 2014)

The comparison of the two tests shows that the process works much better if it ran for more time in spite of the higher concentrations.

12 Discussion and Conclusions

A full scale shower wastewater recycling system has been laboratory tested to determine if it merits further investigation and development for public use. On the basis of the results of the study, it can be concluded that the shower loop works effectively in removing the hardness of the shower water as well as potassium levels. The pH, conductivity levels and the turbidity levels also prove the conclusion that the system works and it is very effective and worth installing. The treatment equipment, the automation and process are compatible with the conventional shower facilities thus not needing extra supplies. The use of sand and activated carbon filter as well as UV system works well and it is effective in removing fluoride and some amount of sulphate is removed from the system. However, more testing and thorough investigation of activated carbon would help to better the results.

12.1 Future research and recommendation

Further research is needed to understand the effect of individual items like sand and activated carbon to determine which one has larger effect in the removal process. The use of temperature sensors in each of the level i.e. before the process, after the ac, after the sand and after the UV, could be beneficial for understanding the role of temperature in the removal process.

Table 25 shows that the phosphate level exceeded with a larger amount (+0.56 mg/l). The higher level of phosphate stimulates the growth of phytoplanktons and algae. The higher level of these phosphates acts as a nutrient for the growth of plants in the sand or activated carbon.

12.1.1 Chemical solutions

In order to protect such effects, some solutions could be the addition of Alum or hydrated aluminium sulphate to precipitate phosphate and aluminium phosphates (AlPO4). The basic reaction is

$$Al^{3+} + H_nPO_4{}^{3-n} \leftarrow\rightarrow AlPO_4 + nH^+$$

The addition of aluminium dosage is dependent on the pH, alkalinity, trace elements found in the process water. The dosage rate is the function of the phosphorus removal required. The efficiency of coagulation falls as the concentration of phosphorus decreases. An efficiency of 80-90 % can be reached with 50-200 mg/l dosage. A second option would be to be the addition of Ferric chloride or sulphate and ferrous sulphate. Ferric ions combine to form ferric phosphates which would then precipitate. The basic reaction is as follows:

$$Fe^{3+} + HnPO_4{}^{3-n} \leftarrow\rightarrow FePO_4 + nH^+$$

12.1.2 Non- chemical solutions

A non-chemical solution is to change the activated carbon from a source that has no or reduced amount of phosphate and potassium in it. Since, the performance of the activated carbon depends on its formation, changing the activated carbon could help the overall process efficiency and reduce the formation of phosphates as well as increase potassium adsorption.

12.1.3 Real life samples

The samples that were made for the tests only had shampoo in it, whereas in real life the bathing water contains hair, skin, shampoo, and many other elements; thus, to tests these elements in the process, real life samples should be taken. The data from those tests then would be compared to this data to see the similarities or dissimilarities.

13 References

Kupchella, C. and Hyland, M, 1993. *Environmental science*. Englewood Cliffs, N.J.: Prentice Hall.

Gleick, P, 1986. Methods for evaluating the regional hydrologic impacts of global climatic changes. *Journal of Hydrology*, 88(1-2), pp.97-116.

Nkwonta, O., Olufayo, O., Ochieng, G., Adeyemo, J. and Otieno, F, 2010. Turbidity removal: Gravel and charcoal as roughing filtration media. *South African Journal of Science*, 106(11/12).

Selvarajan, J. and Holland, K, 2013. ShowerMagic : *A Hygienic and Eco-Efficient Real Time Greywater Reuse System for Showers*. Metropolia Ammattikorkeakoulu. [online] Available at: http://www.theseus.fi/handle/10024/76148 [Accessed 17 Mar. 2015].

Mattson, J. and Mark, H, 1971. *Activated carbon: surface chemistry and adsorption from solution*. New York: M. Dekker.

Van Winkle, S, 2000. *The effect of activated carbon on the organic and elemental composition of plant tissue culture medium*. Institute of Paper Science and Technology. Atlanta, Georgia, May, 2000

Google Books, 2015. *A Review of the U.S. Army Construction Engineering Research Laboratory Program for Recycling and Reuse of Laundry and Shower Wastewater*. [online] Available at: http://books.google.fi/books?id=q2ArAAAAYAAJ&pg=PA6&lpg=PA6&dq=water+quality+standards+for+shower&source=bl&ots=8vuWYmx6AC&sig=nu-Fi7gDlI0OPYIpqEE7WIMPS2w&hl=en&sa=X&ei=At1IVMiLGKP4yQO-

9IHQDw&ved=0CEAQ6AEwAw#v=onepage&q=water%20quality%20standards%20for%20shower&f=false [Accessed 17 Mar. 2015].

Mäkinen, R, 2008. *Drinking water quality and network materials in Finland*. 1st ed. [ebook] Finnish Institute of Drinking Water. Available at: http://www.samk.fi/download/27214_Summary.pdf [Accessed 17 Mar. 2015].

Water.epa.gov, 2015. *5.4 pH* | *Monitoring & Assessment* | US EPA. [online] Available at: http://water.epa.gov/type/rsl/monitoring/vms54.cfm [Accessed 30 Mar. 2015].

U.S. Environmental Protection Agency (EPA). (2011) *Exposure Factors Handboo*k: 2011 Edition. [ebook] National Center for Environmental Assessment, Washington, DC; EPA/600/R-09/052F. Available at National Technical Information Service, Springfield, VA. [online] Available at http://www.epa.gov/ncea/efh/pdfs/efh-complete.pdf [Accessed 18 Mar. 2015]

Water.epa.gov, 2015. *Conductivity* | *Monitoring & Assessment* | US EPA. [online] Available at: http://water.epa.gov/type/rsl/monitoring/vms59.cfm [Accessed 18 Mar. 2015].

Lenntech.com, 2015. *Water conductivity* - Lenntech. [online] Available at: http://www.lenntech.com/applications/ultrapure/conductivity/water-conductivity.htm [Accessed 18 Mar. 2015].

Systems, M, 2015. *Conductivity Measurement and Theory*. [online] Mbhes.com. Available at: http://www.mbhes.com/conductivity_measurement.htm [Accessed 18 Mar. 2015].

Gatenby, A, 2015. *Surface Tension by duNouy Rings or Wilhelmy Plates – Which to Choose?*. [online] Cscscientific.com. Available at: http://www.cscscientific.com/csc-cientific-blog/bid/45263/Surface-Tension-by-duNouy-Rings-or-Wilhelmy-Plates-Which-to-Choose [Accessed 18 Mar. 2015].

Lenntech.com, 2015. *Turbidity.* [online] Available at: http://www.lenntech.com/turbidity.htm#ixzz3R3yPreK7 [Accessed 17 Mar. 2015].

Pca.state.mn.us, 2015. *Turbidity: Description, Impact on Water Quality, Sources, Measures.* [online] Available at: http://www.pca.state.mn.us/index.php/view-document.html?gid=7854 [Accessed 17 Mar. 2015].

John Gregory, 1988, *Turbidity and beyond, Filtration & Separation*, Volume 35, Issue 1, January–February 1998, Pages 63-67, ISSN 0015-1882, http://dx.doi.org/10.1016/S0015-1882(97)83117-5. Available at http://www.sciencedirect.com/science/article/pii/S0015188297831175

Ritter, J, 2010. *Water Quality.* 4th ed. [ebook] Denver, CO, USA: American Water Works Association. Available at: http://site.ebrary.com/lib/metropolia/docDetail.action?docID=10533523 ER - [Accessed 17 Mar. 2015].

Brown, P. and Grushka, E, 2001. *Advances in chromatography*. Vol.41. New York: Marcel Dekker. 1006-1012

Metrohm.com, 2015. *Instruments.* [online] Available at: http://www.metrohm.com/com/Support/Technical_Documents/Instruments.html?identifier=761&language=en&name=761+Compact+IC [Accessed 3 Mar. 2015].

Kellner, R, 1998. *Analytical chemistry*. Weinheim [Federal Republic of Germany]: Wiley-VCH.
Poole, C, 2003. *The essence of chromatography*. Amsterdam: Elsevier 269-298

Scott, R, 1995. *Techniques and practice of chromatography*. New York: M. Dekker.

Quality, U, 2015. *USGS Water-Quality Information: Water Hardness and Alkalinity*. [online] Water.usgs.gov. Available at: http://water.usgs.gov/owq/hardness-alkalinity.html [Accessed 17 Mar. 2015].

Whqlibdoc.who.int, 2011. *Potassium in drinking-water*. [online] Available at: http://whqlibdoc.who.int/hq/2009/WHO_HSE_WSH_09.01_7_eng.pdf [Accessed 2 Apr. 2015].

Whqlibdoc.who.int, 2011. *Guidelines for Drinking-water Quality*. [online] Available at: http://whqlibdoc.who.int/publications/2011/9789241548151_eng.pdf?ua=1 [Accessed 2 Apr. 2015].

Dulal, B. 2014. *Nutrient Limitation of Phytoplankton in Helsinki Coastal Region*. 1st ed. [ebook] vantaa: Metropolia Ammattikorkeakoulu. Available at: http://www.theseus.fi/handle/10024/77896 [Accessed 23 Apr. 2015].
Itl.nist.gov,. '5.7. A Glossary Of DOE Terminology'. N.p., 2015. Web. 23 Apr. 2015.

Berthouex, P. and Brown, L, 2002. *Statistics for environmental engineers*. Boca Raton: Lewis Publishers.

Cran.r.project.org, 2015. *Package 'GAD'.* [online] Available at: http://cran.r-project.org/web/packages/GAD/GAD.pdf [Accessed 1 May 2015].

A. **Appendix 1.** Coumpounds found in shower water quality

Table 26. Compounds found in the shower water quality that are less than 0.2 mg/l.

Alumina
Aluminium chloride
Aluminium sulfate
Beeswax
Boric acid
Cetyl alcohol
Corn starch
Bentonite
Hexachlorophene
Isopropyl myristate
Magnesium carbonate
Magnesium oxide
Glycerol monosterate
Methyl paraben
Lanolin
Petrolatum
PABA
Isopropyl palmitate
Polyethylene sorbitan mono sterate
Saccharin sodium
Sodium-6-chloro-2-phenyl-phenolate
Sodium hydroxide
Sorbitol
Spermaceti
Sorbitan monosterate
Stannous fluoride
Veegum
Zinc chloride
Sodium sterate

Appendix 2. Technical Data for MP AES

Table 27. General settings for all elements for MP-AES

Settings	**Note**
Replicates	3
Calibration Correlation Coefficient Limit	0.9
Pump Speed (rpm)	15
Blank Subtraction	On
Sample introduction	Manual
Stabilization time (s)	15
Sample Uptake Time(s)	15
Sample uptake fast pump	On
Rinse time (s)	N/a
Rinse time fast pump	N/a
Air Injection mode	Off
Standard addition	Off
Reagent blank	Off
QC Active	Off
Reslope	Off

Appendix 3. Technical Data for Metrohm IC 761

A. Conductivity detector

Table 28. Technical data for conductivity detector for metrohm IC 761

Construction	Thermostatted conductivity dector with 2 ring-shaped steel electrodes
Measurement principle	Alternating current measurement with 1KHz frequency and ca 1.7 V amplitude (peak to peak)
Cell volume	1.5 µL
Cell constant	Approx. 17 / cm
Maximum back pressure for measuring cell	5 MPa
Thermostatting	Connectable dynamic control to adjustable operating temperature
Operating temperature	Adjustable insteps of 5 °C from 25…45 °C
Max. temperature deviation	± 2,5 ° C
Heating time	≥ 30 min
Temperature stability	≤ 0.01 C at constant ambient temperature
Connection for detector block	Dsub 15 pin (female)

B. High pressure pump

Table 29. Technical data for High pressure pump for Metrohm IC 761

Type	**Serial dual piston pump with two valves**
Pump capacity	
Flow range	0.20..2.5 mL/ min
Maximum error	< ± 2% of set value
Flow constancy	< 0.5 % of set value
Reproducibility of eluent flow	Typ. Better than ± 0.1%
Pressure measurement	
Pressure range	0…25 MPa

Type	**Serial dual piston pump with two valves**
Residual pulsation	< 1% (at 1 mL /min water and 10 MPa pressure, without pulsation dampener)
Maximum error	± 3 % of set value
Resolution	0.1 MPa (conductivity measurements) 0.001 MPa (pressure measurements)
Sampling rate	1 measurement /piston stroke (pump running) 1 measurement/s (pump not running) 10 measurements (pressure measurements)
Safety shutdown	
Function	Automatic shutdown when upper and lower pressure limits violated
Maximum pressure limit	Adjustable between 0.1.. 25 MPa Response time: 1 pump cycle
Minimum pressure limit	Adjustable between 0.1.. 25 MPa Response time: 5 pump cycles
Pump head	
Pump head volumes	Main piston 40 μL Priming piston 20 μL
Pump displacement volumes	Main piston 28.5 μL Priming piston 14.25 μL
Length of stroke	Main piston 3.6 mm Priming piston 1.8 mm

C. Peristaltic pump

Table 30. Technical data for peristaltic pump for Metrohm IC 761

Type	**2- channel peristaltic pump**
Pump capacity	
Rotational speed	20 U/min at 50 Hz 24 U/min at 60 Hz

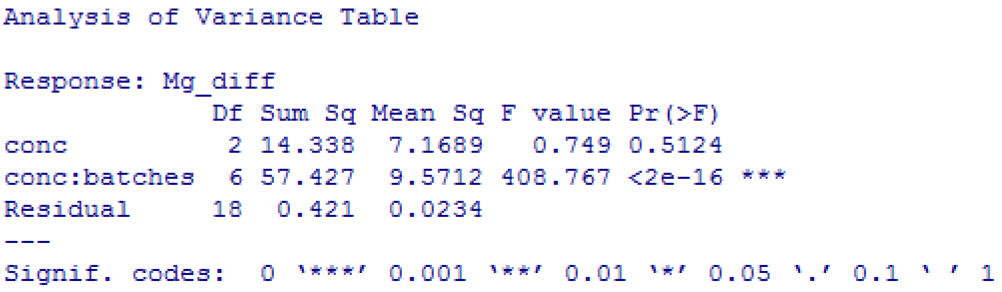
Type	**2- channel peristaltic pump**
Flow range	0.5.. 0.6 mL/min with 6.1826.060 pump tubing
Maximum error	± 5 %
Maximum pressure	0.4 MPa
Pumpable liquids	Clear liquids with no solid content
Pump tubing material	PP (polypropylene)

Appendix 4. R script for Anova and box plots

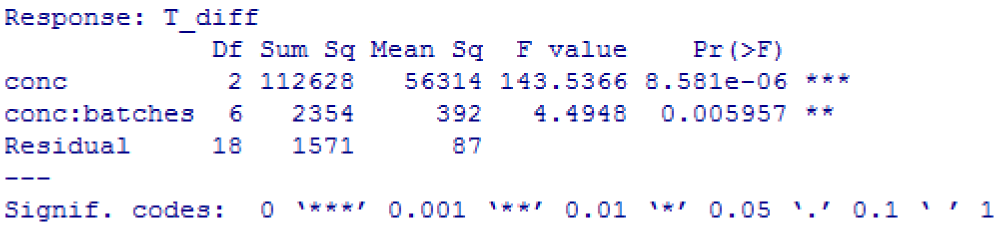
```
#install(GAD)
data1    <- read.table('test.txt',header=TRUE)
names(data1)
conc     <- as.fixed(data1$Conc)
batches  <- as.random(data1$B)
is.fixed(conc) #check if conc is fixed or not
is.random(batches)#check if batches are random or not
Cl_diff <- Cl_in-Cl_out
model1   <- lm( Cl_diff ~ conc + batches%in%conc , data=data1)
print(gad(model1))
print(C.test(model1)) #homogeneity of variances

print(estimates(model1))
snk_test_interaction <- snk.test(model1,term = 'conc:batches', among = 'batches', with-
in = 'conc') #check which batches are significant
graphics.off ()
snk_test_concentration <-snk.test(model1,term = 'conc', among ='conc',within
='batches') # check which concentration level is significant

windows()
plot(as.factor(conc:batches),Cl_diff)

b=as.matrix(Cl_diff)

windows()


boxplot(b[1:3], b[4:6],b[7:9,], b[10:12], b[13:15], b[16:18], b[19:21], b[22:24],
b[25:27],xlab="batches with added concentration",ylab="Cl_diff(mg)",
col=terrain.colors(3), las = 2, names =
c("5ml","5ml","5ml","10ml","10ml","10ml","15ml","15ml","15ml"),at =c(1,2,3, 6,7,8,
11,12,13), main="Boxplot by batches and concentration")
legend("topleft", inset=.02, title="Batches",
                    c("1","2","3"), fill=terrain.colors(3),)
```

Appendix 5. Summary tables of the anova

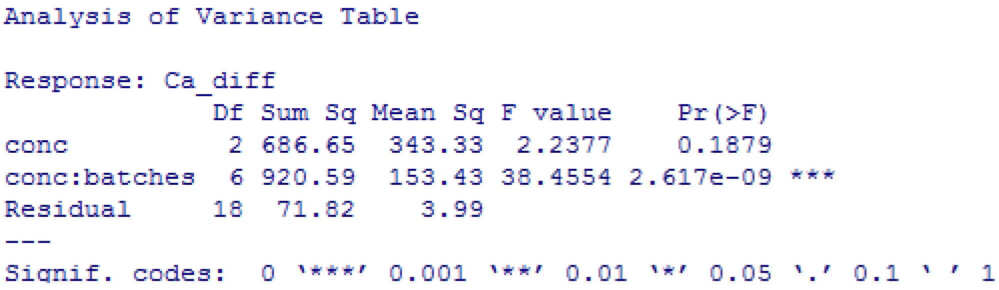
Figure 30 shows the summary of the anova table for all of the elements that are not mentioned in the thesis.



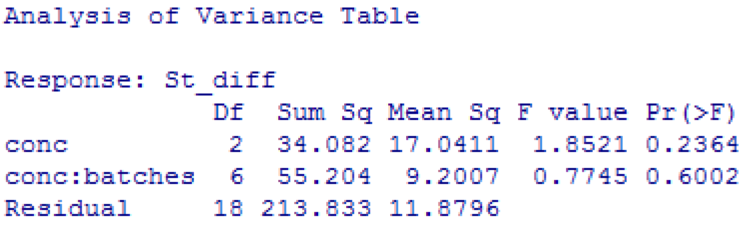
```
Analysis of Variance Table

Response: Mg_diff
             Df Sum Sq Mean Sq F value Pr(>F)
conc          2 14.338  7.1689   0.749 0.5124
conc:batches  6 57.427  9.5712 408.767 <2e-16 ***
Residual     18  0.421  0.0234
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```



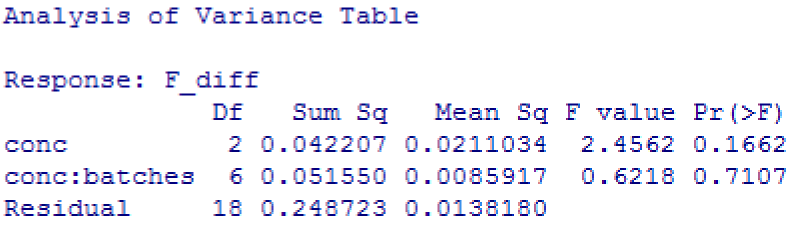
```
Response: T_diff
             Df Sum Sq Mean Sq  F value    Pr(>F)
conc          2 112628   56314 143.5366 8.581e-06 ***
conc:batches  6   2354     392   4.4948  0.005957 **
Residual     18   1571      87
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```



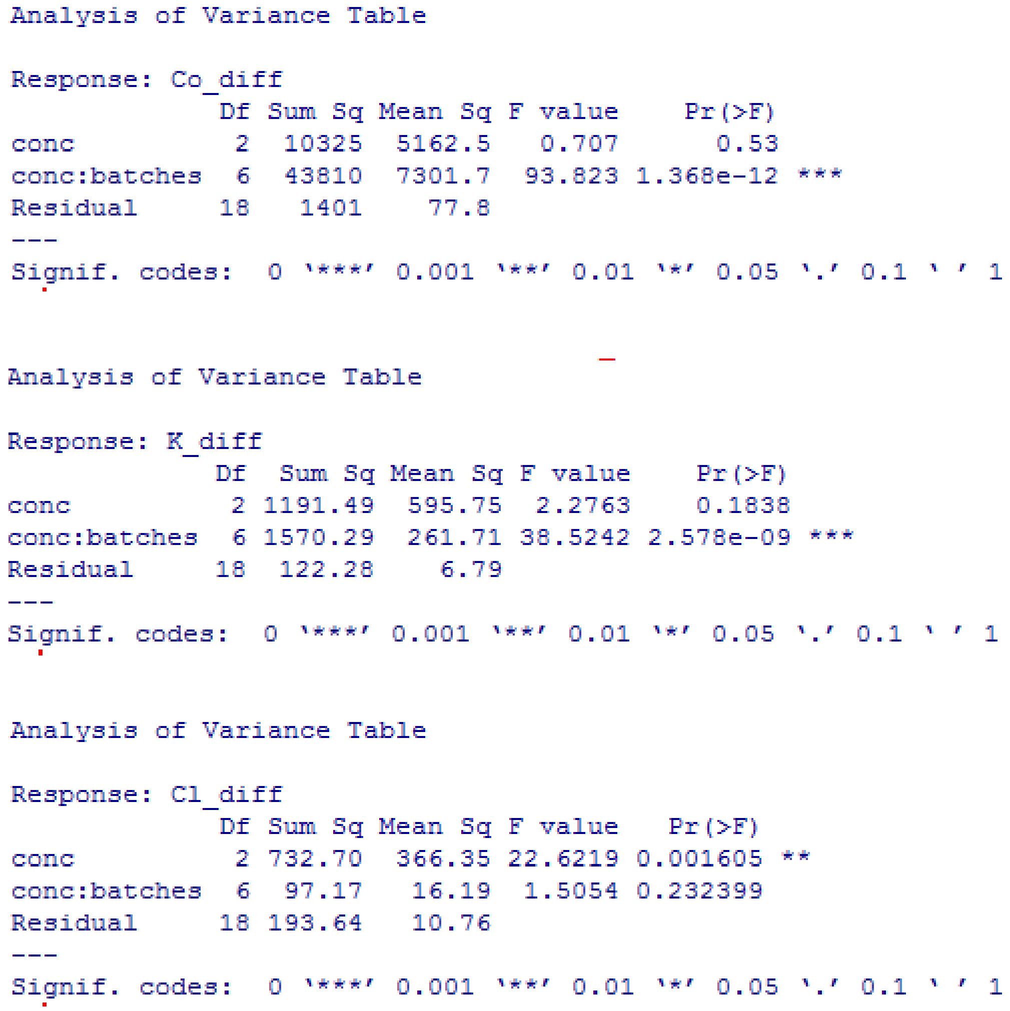
```
Analysis of Variance Table

Response: Ca_diff
             Df Sum Sq Mean Sq F value    Pr(>F)
conc          2 686.65  343.33  2.2377    0.1879
conc:batches  6 920.59  153.43 38.4554 2.617e-09 ***
Residual     18  71.82    3.99
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```



```
Analysis of Variance Table

Response: St_diff
             Df  Sum Sq Mean Sq F value Pr(>F)
conc          2  34.082 17.0411  1.8521 0.2364
conc:batches  6  55.204  9.2007  0.7745 0.6002
Residual     18 213.833 11.8796
```



```
Analysis of Variance Table

Response: F_diff
             Df   Sum Sq   Mean Sq F value Pr(>F)
conc          2 0.042207 0.0211034  2.4562 0.1662
conc:batches  6 0.051550 0.0085917  0.6218 0.7107
Residual     18 0.248723 0.0138180
```



```
Analysis of Variance Table

Response: Co_diff
             Df Sum Sq Mean Sq F value    Pr(>F)
conc          2  10325  5162.5   0.707      0.53
conc:batches  6  43810  7301.7  93.823 1.368e-12 ***
Residual     18   1401    77.8
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1


Analysis of Variance Table

Response: K_diff
             Df  Sum Sq Mean Sq F value    Pr(>F)
conc          2 1191.49  595.75  2.2763    0.1838
conc:batches  6 1570.29  261.71 38.5242 2.578e-09 ***
Residual     18  122.28    6.79
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1


Analysis of Variance Table

Response: Cl_diff
             Df Sum Sq Mean Sq F value   Pr(>F)
conc          2 732.70  366.35 22.6219 0.001605 **
conc:batches  6  97.17   16.19  1.5054 0.232399
Residual     18 193.64   10.76
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Figure 30. Summary table of anova of the difference for the measured elements..

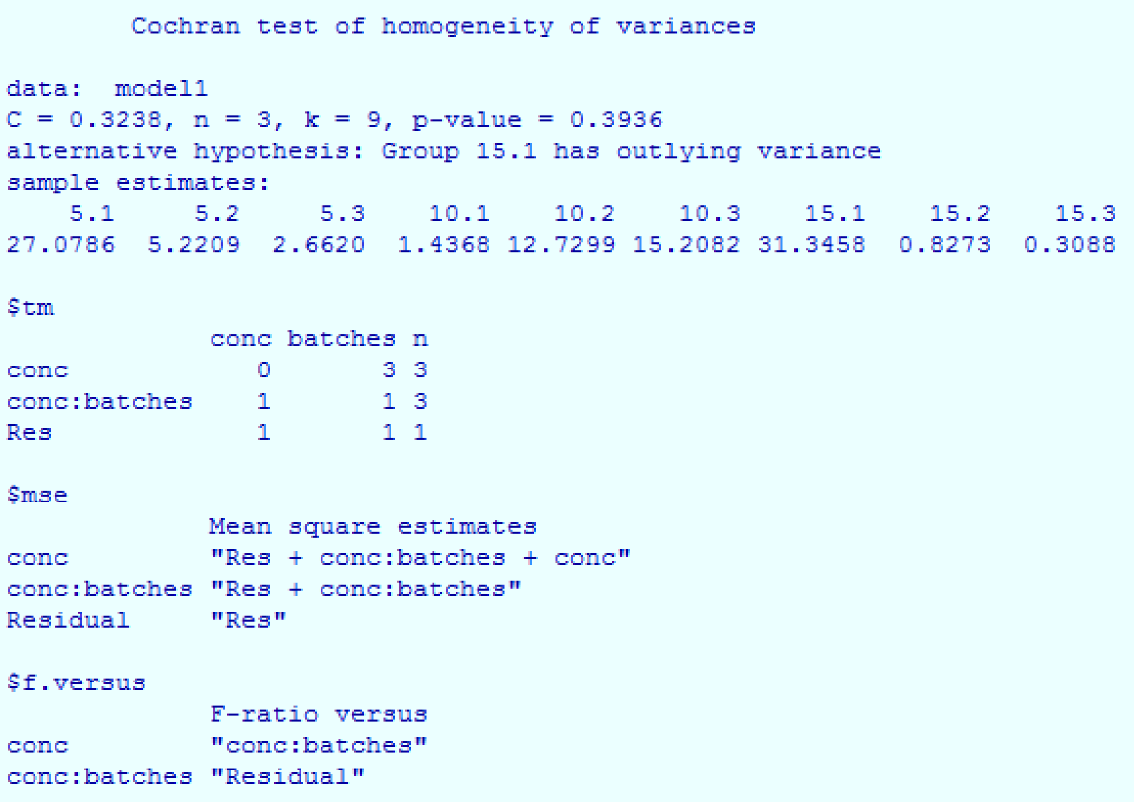
Appendix 6. Cochran's test of homogeneity

The C test is used to decide if a single estimate of a variance (or a standard deviation) is significantly larger than a group of variances (or standard deviations) with which the single estimate is supposed to be comparable.

R script: print(C.test(model1))

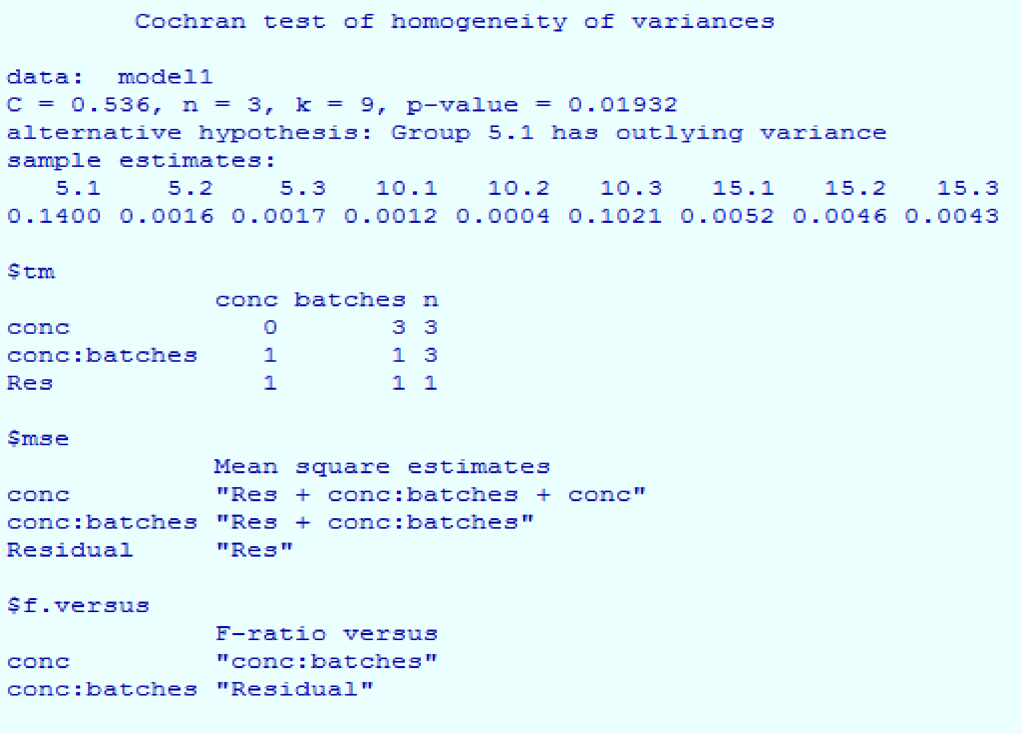
Example:

	Variances are equal /	



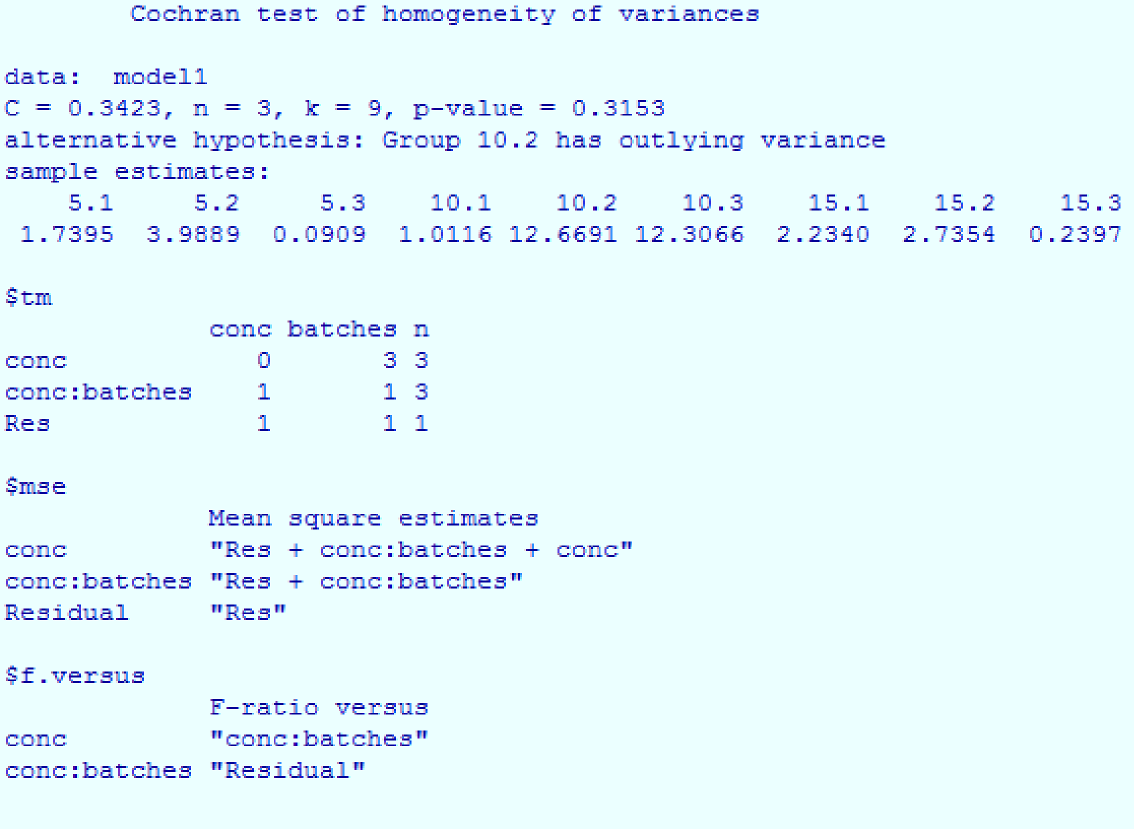
```
        Cochran test of homogeneity of variances

data:  model1
C = 0.3238, n = 3, k = 9, p-value = 0.3936
alternative hypothesis: Group 15.1 has outlying variance
sample estimates:
    5.1     5.2     5.3    10.1    10.2    10.3    15.1    15.2    15.3
27.0786  5.2209  2.6620  1.4368 12.7299 15.2082 31.3458  0.8273  0.3088

$tm
             conc batches n
conc            0       3 3
conc:batches    1       1 3
Res             1       1 1

$mse
             Mean square estimates
conc         "Res + conc:batches + conc"
conc:batches "Res + conc:batches"
Residual     "Res"

$f.versus
             F-ratio versus
conc         "conc:batches"
conc:batches "Residual"
```

Figure 31. C test for Cl_diff



```
        Cochran test of homogeneity of variances

data:  model1
C = 0.536, n = 3, k = 9, p-value = 0.01932
alternative hypothesis: Group 5.1 has outlying variance
sample estimates:
   5.1    5.2    5.3   10.1   10.2   10.3   15.1   15.2   15.3
0.1400 0.0016 0.0017 0.0012 0.0004 0.1021 0.0052 0.0046 0.0043

$tm
             conc batches n
conc            0       3 3
conc:batches    1       1 3
Res             1       1 1

$mse
             Mean square estimates
conc         "Res + conc:batches + conc"
conc:batches "Res + conc:batches"
Residual     "Res"

$f.versus
             F-ratio versus
conc         "conc:batches"
conc:batches "Residual"
```

Figure 32. C test for PO4_diff

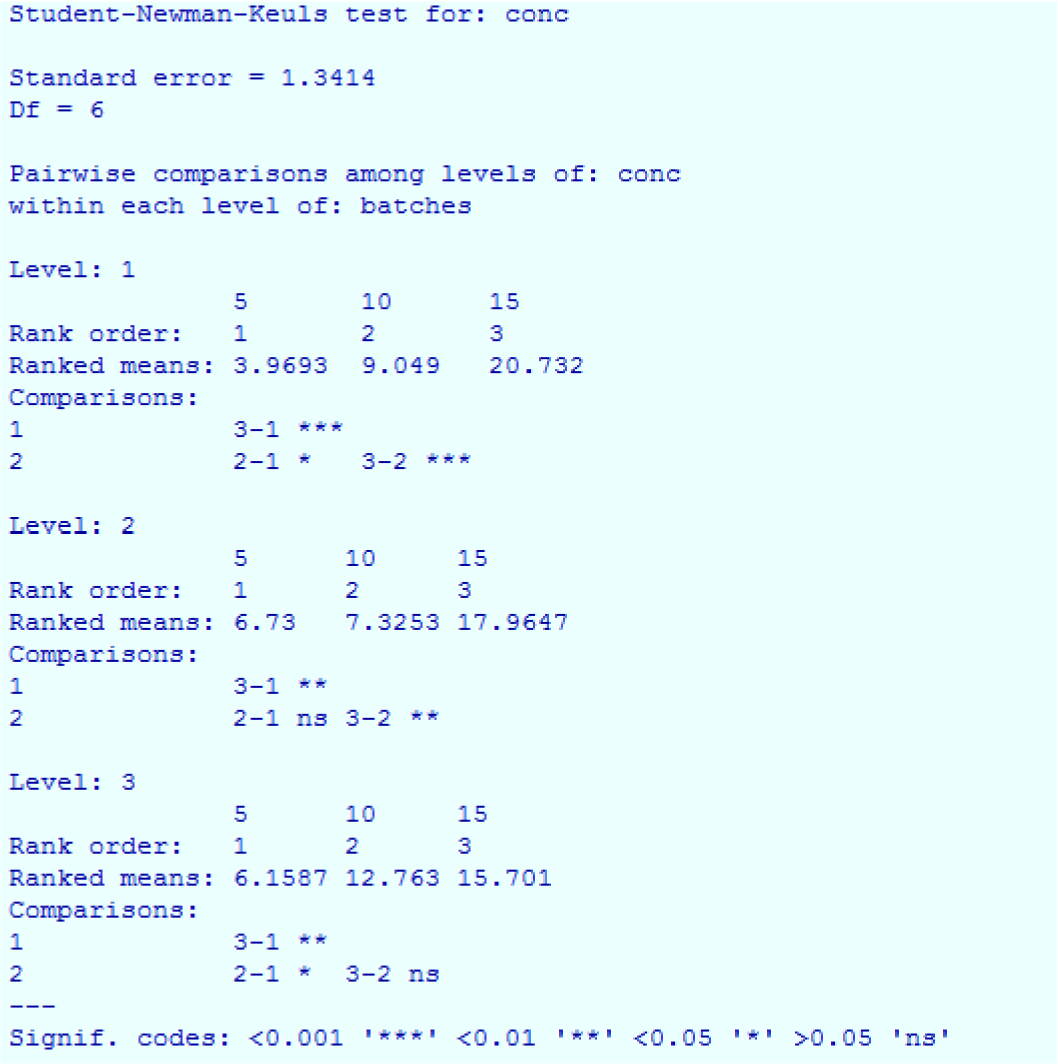


```
        Cochran test of homogeneity of variances

data:  model1
C = 0.3423, n = 3, k = 9, p-value = 0.3153
alternative hypothesis: Group 10.2 has outlying variance
sample estimates:
    5.1     5.2     5.3    10.1    10.2    10.3    15.1    15.2    15.3
 1.7395  3.9889  0.0909  1.0116 12.6691 12.3066  2.2340  2.7354  0.2397

$tm
             conc batches n
conc            0       3 3
conc:batches    1       1 3
Res             1       1 1

$mse
             Mean square estimates
conc         "Res + conc:batches + conc"
conc:batches "Res + conc:batches"
Residual     "Res"

$f.versus
             F-ratio versus
conc         "conc:batches"
conc:batches "Residual"
```

Figure 33. C test for SO4_diff

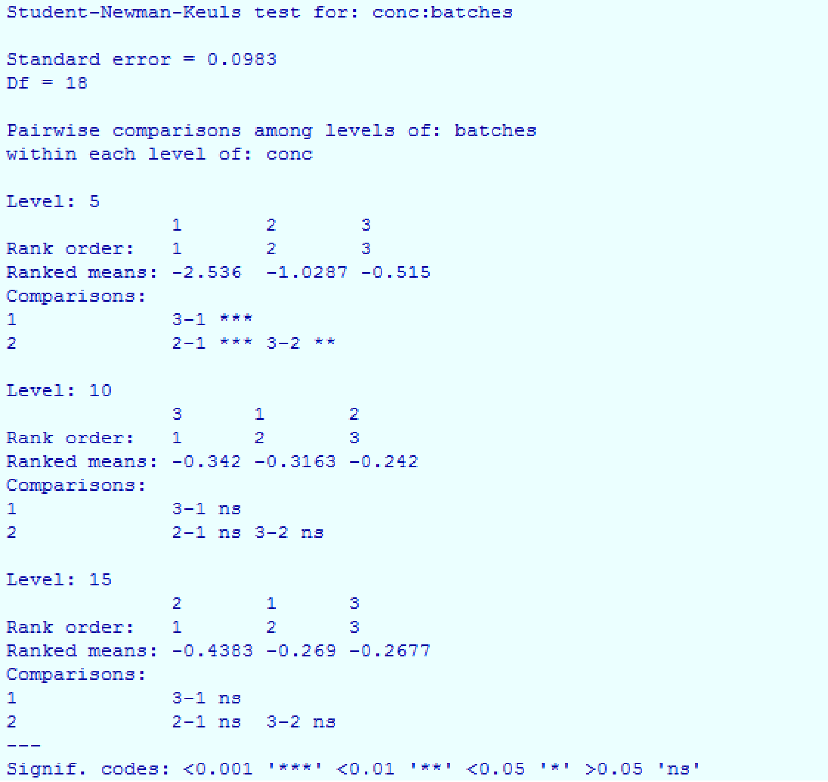
Appendix 7. Student–Newman–Keuls (SNK)

The Newman–Keuls or Student–Newman–Keuls (SNK) method is a stepwise multiple comparisons procedure used to identify sample means that are significantly different from each other.



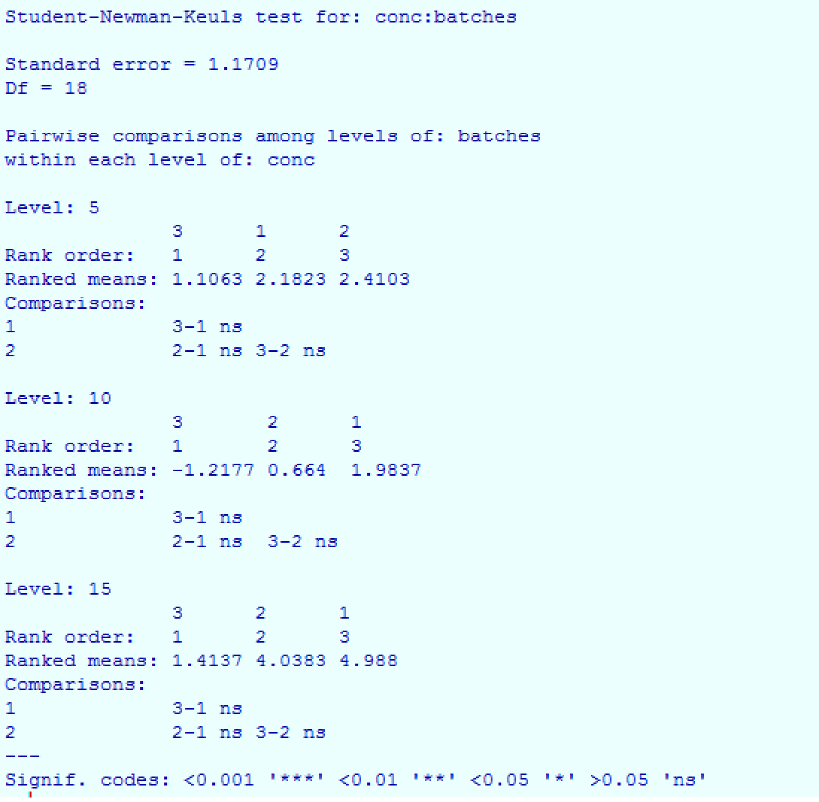
```
Student-Newman-Keuls test for: conc

Standard error = 1.3414
Df = 6

Pairwise comparisons among levels of: conc
within each level of: batches

Level: 1
              5       10      15
Rank order:   1       2       3
Ranked means: 3.9693  9.049   20.732
Comparisons:
1             3-1 ***
2             2-1 *   3-2 ***

Level: 2
              5      10     15
Rank order:   1      2      3
Ranked means: 6.73   7.3253 17.9647
Comparisons:
1             3-1 **
2             2-1 ns 3-2 **

Level: 3
              5      10     15
Rank order:   1      2      3
Ranked means: 6.1587 12.763 15.701
Comparisons:
1             3-1 **
2             2-1 *  3-2 ns
---
Signif. codes: <0.001 '***' <0.01 '**' <0.05 '*' >0.05 'ns'
```

Figure 34. SNK test for Cl_diff



```
Student-Newman-Keuls test for: conc:batches

Standard error = 0.0983
Df = 18

Pairwise comparisons among levels of: batches
within each level of: conc

Level: 5
              1       2       3
Rank order:   1       2       3
Ranked means: -2.536  -1.0287 -0.515
Comparisons:
1             3-1 ***
2             2-1 *** 3-2 **

Level: 10
              3      1       2
Rank order:   1      2       3
Ranked means: -0.342 -0.3163 -0.242
Comparisons:
1             3-1 ns
2             2-1 ns 3-2 ns

Level: 15
              2       1      3
Rank order:   1       2      3
Ranked means: -0.4383 -0.269 -0.2677
Comparisons:
1             3-1 ns
2             2-1 ns  3-2 ns
---
Signif. codes: <0.001 '***' <0.01 '**' <0.05 '*' >0.05 'ns'
```

Figure 35. SNK test for PO4_diff



```
Student-Newman-Keuls test for: conc:batches

Standard error = 1.1709
Df = 18

Pairwise comparisons among levels of: batches
within each level of: conc

Level: 5
              3      1      2
Rank order:   1      2      3
Ranked means: 1.1063 2.1823 2.4103
Comparisons:
1             3-1 ns
2             2-1 ns 3-2 ns

Level: 10
              3       2      1
Rank order:   1       2      3
Ranked means: -1.2177 0.664  1.9837
Comparisons:
1             3-1 ns
2             2-1 ns  3-2 ns

Level: 15
              3      2      1
Rank order:   1      2      3
Ranked means: 1.4137 4.0383 4.988
Comparisons:
1             3-1 ns
2             2-1 ns 3-2 ns
---
Signif. codes: <0.001 '***' <0.01 '**' <0.05 '*' >0.05 'ns'
```

Figure 36. SNK test for SO4_diff