Ultrapure water - a revolutionary cleaning product?

Hanna Andersson
Fiber and Polymer Technology, KTH
2023-05-01
Supervisors: Torbjörn Pettersson and Pär Svahnberg
Examiner: Torbjörn Pettersson

Table of content

Abstract

Soap has been manufactured for over 5000 years and the chemical component responsible for its cleaning properties have persisted till this day - surfactants. Surfactants are amphiphilic molecules that enable the solvation of fat while still soluble in water, making them highly suitable as detergents. However, as some surfactants may be both persistent in nature and toxic to aquatic life, they pose a threat to the environment. Hence, there is a need for environmentally friendly cleaning technologies, possibly without surfactants. Recent research has been on the use of ultrapure water in terms of cleaning textiles and surfaces. Ultrapure water (UPW) is today widely used as a "cleaning solution" within the production of semiconductors and microelectronics, where it desorbs particles from produced micro devices. Hence, highly purified water holds certain "cleaning effects" as the water does not typically prefer being ultra pure and will act to reach a more contaminated state. In fact, successful practical applications, in terms of cleaning textiles and surfaces using UPW, have been reported. Yet, the actual cleaning mechanisms are still unknown. UPW is also used when producing "super alkaline ionized water" (SAIW), another cleaning solution in the UPW family, essentially containing ultrapure water and lye. This work aimed to further investigate the cleaning effects of UPW in terms of cleaning textiles and surfaces as well as its cleaning effects in comparison to SAIW, traditional detergents and most importantly to tap water. Could UPW be a significantly better cleaning agent than tap water?

These questions were evaluated via different tests, mainly simulating the cleaning of textiles and surfaces. Laundry tests were performed in commercial laundry machines, following the *EN 60456:2016* standard, including soil removal evaluation via reflectance measurements. Surface cleaning tests were done using QCM-D analysis. Furthermore, cleaning tests of individual fibers followed by optical microscopy and emulsion tests were done to visualize cleaning mechanisms in real time. The results within this study suggest that the cleaning effects of UPW alone is not different compared to the cleaning effect of regular tap water. Even though there is promising scientific research documenting the cleaning potential of UPW, it needs further investigations and research to understand its cleaning performance. Traditional detergents, based on surfactants, showed the overall best cleaning effects in all tests performed in this study.

Sammanfattning

Tvål har tillverkats i över 5000 år och likaså har den kemiska komponenten bakom dess effekt inte ändrats - nämligen tensider. Tensider är amfifila molekyler som kan lösa både fett och vatten, vilket gör dem speciellt lämpliga som ingrediens i tvättmedel. Dock kan tensider vara både svårnedbrytbara i naturen och giftiga för vattenlevande organismer, så dessa utgör ett hot mot miljön. Således finns det ett behov för en miljövänlig tvätt-teknologi, möjligtvis utan tensider.
Det har utförts forskning på ultrarent vatten för tvätt av textilier och ytor. Ultrarent vatten används även idag som "rengöringsmedel" vid produktion av halvledare och mikroelektronik, där det används för att desorbera partiklar från materialet under vissa produktionssteg. Följaktligen har högrent vatten en viss "rengörande effekt" som en följd av att vatten generellt inte vill vara rent utan kommer att sträva mot ett mer mättat tillstånd. Det har nyligen genomförts framgångsrika försök med ultrarent vatten vid rengöring av textilier och olika ytor. Däremot är mekanismerna bakom dess rengörande effekt fortfarande okända. Ultrarent vatten används även som en komponent vid framställningen av ett annat rengöringsmedel, nämligen "super alkaline ionized water" (SAIW), vilket i själva verket är en blandning av ultrarent vatten och lut.
Syftet med denna rapport är att utvärdera de rengörande effekterna av ultrarent vatten i samband med tvätt av textilier och ytor. Likaså jämförs dess rengörande effekter med SAIW, traditionella tvättmedel och framförallt med vanligt kranvatten. Är ultrarent vatten ett signifikant bättre rengöringsmedel än kranvatten? För att besvara dessa frågor har flera simulerade tester, för att efterlikna framförallt tvätt av textilier och ytor, genomförts. Tvätt-tester av textilier har genomförts i kommersiella tvättmaskiner, enligt standarden *EN 60456:2016*, där fläckborttagnings-förmåga utvärderats med reflektans-mätningar. Ytrengörings-tester genomfördes med QCM-D-mätningar. Tvätt-tester på enstaka fibrer följt av optisk mikroskopi och emulsionstest genomfördes för att visualisera rengöring i realtid. Resultaten i den här studien tyder på att de rengörande effekterna av ultrarent vatten är likställda med effekten av vanligt kranvatten. Trots att det finns lovande vetenskaplig data för den rengörande effekten av ultrarent vatten så behövs mer forskning inom området. Traditionella rengöringsmedel, med tensider, visade sig ha den bästa rengörande förmågan i alla tester i den här studien.

Acknowledgements
Thank you to Kemitekniska Företagen and Toxintelligence for presenting the idea and for supporting me with test material and background knowledge. Thank you Torbjörn for supervision, patients and support at KTH. Thank you to Anna, Annie, Ingemar, Fredrik, Tom and Fludivad for phenomenal help and inspiration. Thank you to Maskintjänst Stockholm and PT Professionals Karlskrona for helping me when needed. A special thank you to all my fellow colleagues at KTH which made every day in the lab so much fun.

Abbreviations and explanations

FPT = Fiber and Polymer Technology
MQ water = Milli-Q® water
SAIW = Super alkaline ionized water
SDS = Sodium dodecyl sulphate
UPW = Ultrapure water
QCM-D = Quartz crystal microbalance with dissipation monitoring

1. Introduction

1.1 Cleaning

The purpose of cleaning is simple; undesired compounds are to be eliminated from a surface, such as using dish soap to wash dirt off a plate. What is not as simple is the scientific mechanisms behind a unique cleaning process. Consider the plate example; what material is the plate made of? What is the dish soap made of? What is in the tap water and how warm/cold is it? What is the dirt made of and how do you define clean? Hence, a unique cleaning process alone is highly complex and depends on a wide range of different factors. All these factors need to be considered to fully understand a cleaning process as well as to optimize it.[1]

1.2.1 Cleaning history

Detergents such as soap can be dated back to the third millenium BC (2800 BC) in the ancient Near East, Babylonia. Archeologists have found that clay of that time embedded soap-resembling materials. In addition, the extracted material was marked with a phrase interpreted as “fats boiled with ashes” which happens to be the traditional technique for producing soap.[2][3] The reaction taking place when fats are boiled with ashes is called saponification. This is the hydrolysis of triglycerides in the presence of a strong base, such as one of the major components in ash. The resulting fatty acid salt holds both hydrophobic and hydrophilic parts, a molecule today known as “surface active agent” (surfactant) or soap (Figure 1). Thus, these kind of molecules may surround and trap dirt while diffusing in water - a key property of detergency molecules.[4] Even findings from ancient Egypt demonstrate the use of a material made from animal/vegetable fat and alkaline salts for wash and disease treating purposes.[2][3]

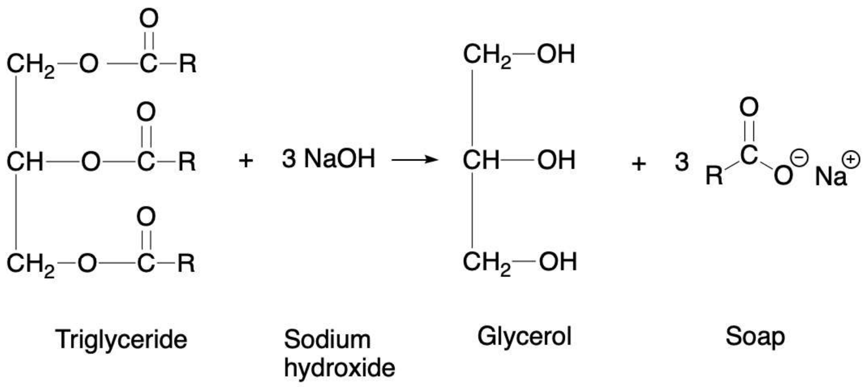

Figure 1. An example of a saponification reaction between a triglyceride and a strong base (NaOH) resulting in soap.

The ways of making soap practically did not change until World War I, as well as during World War II, when a shortage of animal/vegetable fat and oil emerged. The world was in need of a new kind of soap. Thus, chemists began synthesizing raw materials for soap making and synthesized detergents were born.[2][3] The synthetic detergents also contain surfactants, substances which we today would call detergent molecules.[2][3][4] So far, soaps are proposed to have saved hundreds of million lives and counting.[5]

1.2.1 Cleaning theory

Sinner's circle (Figure 2) is a simplified, yet common representation of how the performance of a cleaning process is the result of four main factors; *chemistry, time, mechanical action* and *temperature*. The idea of the circle is to demonstrate that the four factors can be altered/lowered individually as long as the remaining factors match the lowering/altering of that altered part. For example, if temperature is reduced, time/mechanical action or chemistry should be enhanced to maintain the same, or a better, cleaning performance.[1]

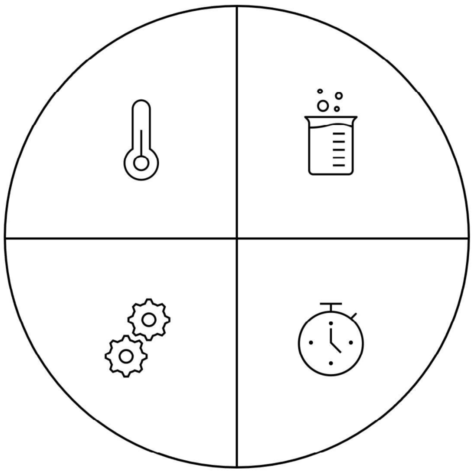

Figure 2. Sinner's circle.

Washing dishes in the sink generally implies a high mechanical action, why there is commonly no need for a long amount of time to achieve a clean result. On the other hand, dishwashing machines generate a relatively low mechanical action hence, dishwasher programs usually require a longer operation time, including more aggressive detergents.[1]

Evidently, a cleaning process is also highly dependent on the type of soil being removed and from what material. Certain materials can not stand high temperatures while others can not stand high mechanical actions. Soils of proteins may be harder to remove at elevated temperatures while high temperatures are efficient against greasy and fatty soils. In short, cleaning in reality is more complex than a circle divided into four pieces can describe, yet every piece may be elaborated and further explained to get a better understanding of the reality.[1]

1.2. Surfactants

Surface active agents (surfactants) are, as the name suggests, molecules that have an impact on a surface. This attribute comes from their amphiphilic nature, holding both hydrophobic and hydrophilic parts, enabling these molecules to act on the surface of water (Figure 3). The amphiphilic property of surfactants is why they can be used as cleaning agents. Though surfactants are of high diversity (anionic, cationic, amphoteric and non-ionic)[6] they all share a hydrophobic tail group and a hydrophilic head group allowing them to assemble into micelles.[4][6] Micelles are spherical aggregates holding a hydrophobic interior and a hydrophilic exterior, all to achieve a low total free energy in the system.[4] The function of micellation is what gives these molecules their detergency and solubilisation attribute.[6]

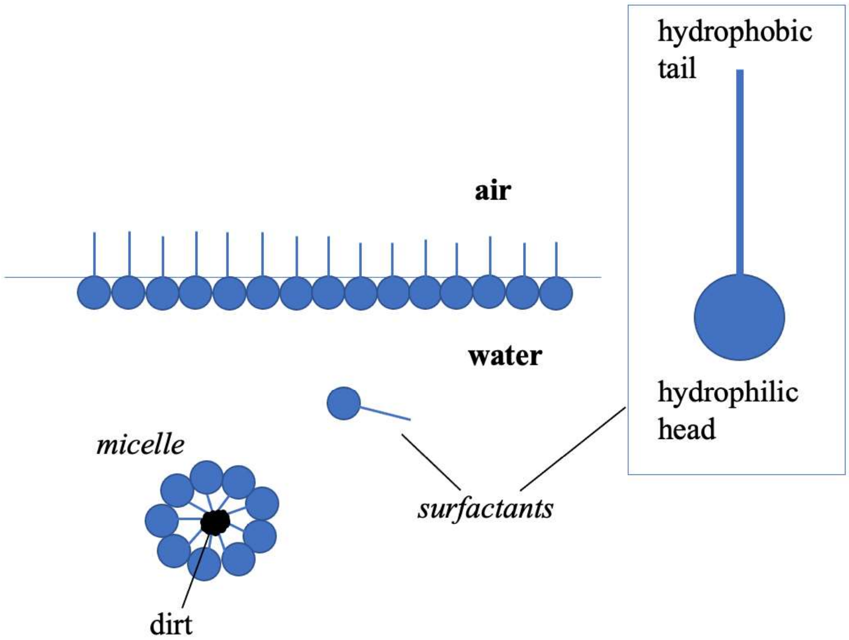

Figure 3. Micellation of surfactants, trapping dirt interiorly.

Surfactants appear as monomers in water when present in low concentrations. As the concentration increases, the critical micelle concentration (CMC) is reached. This is the concentration at which surfactants assemble into micelles. Above CMC, surfactants enable an increased amount of hydrophobic organic compounds in water.[4]

Builders were added to commercial detergents after World War II. Builders are anions capable of separating cations such as those from Magnesium and Calcium naturally present in hard waters. This property is important, otherwise the metal cations will attach to the charged head groups of the surfactants, lowering or hindering their cleaning property.[4]

1.2.1 Environmental challenges

The use of synthetic detergents are not problem free as they may have a negative impact on the environment. Some synthetic surfactants are more or less persistent and accumulate in nature. They can also be toxic to aquatic life as they may interact with biological cell membranes.[4]

The builder material poses other challenges as these are usually made of polyphosphates. Once in water, polyphosphate builders such as triphosphoric acid ($H_5P_3O_{10}$) forms different phosphate ions, This causes a phosphate excess and hypereutrophication which affects ecosystem.[4]

Another issue is the use of nonionic surfactant, alkylphenol ethoxylates as it may degrade into nonylphenol. Nonylphenol is an estrogen endocrine disrupting chemical. According to Directive 2003/53/EC, nonylphenol is restricted for commercial use. The molecule is also categorized as a priority pollutant in Europe.[4]

As traditional detergents are related to several environmental impacts, recent research has been focused on the use of mainly water in terms of cleaning. In fact, successful practical applications have been reported using ultra pure water (UPW), yet the actual cleaning mechanisms are still unknown. Another cleaning agent candidate that has been up for discussion is super alkaline ionized water (SAIW), also known as Z-water.

1.3 Ultra pure water

UPW is a widely used definition of water that has been purified to different levels. While there are standards stating how to classify highly pure water, through contamination levels, there is no accepted definition for UPW. Hence, different industries might claim the consumption of UPW, yet in reality these waters will vary in character depending on the application. However, some features of highly purified water cohere for all industries. Three UPW types commonly aimed for quality laboratory use are Milli-Q®, Elga Ultra and Purite Neptune. Thus, as UPW is mentioned in this paper it may vary in quality.[7]

1.3.1 Characteristics

The purity of water is characterized by its levels of contaminants (such as inorganic/organic matter, microorganisms and dissolved gasses) where, what is commonly known as UPW, should contain no such suspended matter.[8] Theoretically, a value of 100% water purity with no contaminants is achievable yet, it simply can not be maintained. Such water is easily contaminated and eluded when in contact with air, containers and other appliances.[8],[9] Thus, a 100% water purity is not accessible and although a water is said to be of ultrapure character it will hold a certain amount of contaminants.[8]

The electrical conductivity of water is a good measurement for determining its purity since the precise detection of impurities in water is a highly difficult and a time consuming process.[8] The electrical conductivity of water is dependent on the amount of suspended ions and temperature.[8],[9],[10],[11] As the temperature increases, the mobility of ions increase. Interestingly, it has been suggested that the electrical conductivity of water is lowered in the presence of nonpolar gasses disturbing the structure of water. Hence, eliminating all gasses will raise the water conductivity.[12] Furthermore, a rise in temperature will increase the dissociation of water, thus the concentration of ions.[8] The resistivity of theoretically 100% pure water is set to about 18 (MΩ · cm) at 25 °C, originating from the self-dissociation of water ($2H_2O \rightleftharpoons H_3O^+ + OH^-$).[9]

More often than not, UPW is said to obtain a theoretical resistivity value of 18.18 ± 0.03 (MΩ · cm) at 25 °C, resulting in a conductivity of 0,05501 ± 0,0001 µS/cm.[8],[13] Comparatively, tap water holds a conductivity range of 50-500 µS/cm.[7],[11]. However, this range may vary significantly as the quality of tap water highly depends on the geographical location. As the majority of drinking water in the world originates from rivers, lakes and ground waters, the geology of each place will affect the nature of the water.[11]

1.3.2 Production and distribution

The purification of water began around 1945, using ion-exchange resins. Since then, the standard of purified water has only increased [9] and now requires several united purification steps.[8],[14] Among the purification technologies used are electrodeionization, ultrafiltration, reverse osmosis, activated carbon, UV photo-oxidation and ion exchangers.[9],[14],[15].

It is common to build a purification system starting with a preliminary preparation followed by a primary purification step. To guarantee that the system is stable and safe to run, the preliminary preparation should be chosen with respect to the primary purification which in turn will depend on the quality of the local water being purified. As such, primary purification can be a reverse osmosis or an ion exchange while the preliminary preparation can be filtration to prevent fouling in the following purification. Once the water has gone through these steps, essentially all suspended matter and dissolved gasses are eliminated. Then a secondary purification is performed, commonly a UV treatment or ultrafiltration, lowering the levels of contaminants/impurities even further. This step eliminates essentially all microparticles and bacteria and leaves the water ultra pure.[8],[13]

Once purified, the water is to be distributed to the point where it is needed. Since the purified water is "highly reactive" it will dissolve almost everything that comes in its way.[8] Thus, pipes and other appliances of delivery will constitute a risk of contamination and therefore require proper design, where choice of material, flow and pressure is crucial. As mentioned before, it is highly difficult to maintain the purity of the water once it is produced.[8],[13] In fact, it is common to add additional purification steps along the delivery system for UPW intended for the microelectronics.[13]

Furthermore, there are several risks of contamination once the water has reached the point of use. Storing UPW in an open container is impossible as the water will react with the atmosphere.[8],[9] In just a few seconds, water will start solve CO_2 from the air which highly influences the water resistivity due to the production of H_2CO_3. The increased amount of hydronium ions will lower the water resistivity from 18,2 $M\Omega \cdot cm$ to 1,3 $M\Omega \cdot cm$. Moreover, resistivity will decrease when water is stirred or sprayed as these actions will intensify contamination from the atmosphere. Glassware will contribute to alkaline contamination, again affecting the resistivity. Hence, the use and storage of UPW is crucial to keep its properties.[8]

1.3.3 Applications

Ultrapure water is applied in many industries where the required level of purity changes depending on the field of application. In the pharmaceutical industry, UPW is used as injection water where the absence of bacteria and endogenous pyrogen is vital. Ultra pure water is also widely used as cooling water within power engineering operations.[14],[16]. This is in fact the largest use of UPW in the world.[8] Here, UPW helps in corrosion and scaling protection, prolonging the lifetime of power plants.[8][14]

Furthermore, UPW plays a vital role within the production of semiconductors and microelectronics. Here, UPW acts as a cleaning agent, used to desorb particles from the highly contaminant-sensitive manufactured micro/nano devices[8][14],[16]. The purity of water is essential to keep wafers clean as the water otherwise might act as the "contaminator", making the UPW-cleaning of no use.[8] In fact, the production of semiconductors requires a purity equal to 18 MΩ cm (at 25 °C) and elimination of essentially all pollutants. Thus, the production of UPW within the microelectronic industry is the most extensive.[14] However, it has been stated that UPW cleaning method only targets polar and ionic substances, never non-polar, as this type of dissolution is a direct effect of changes in entropy even though the enthalpy changes might be favourable.[9]

UPW is also used as blank water for highly sensitive chemical analysis such as mass spectrometry and liquid chromatography.[8],[16]. Conducting HPLC and LC-MS requires a mobile phase of high purity with an on demand distribution. The level of detection will be greatly influenced by the level of water purity.[8] Hence, UPW is used in a variety of applications and new research suggests further areas of applications.

1.4 Current research on UPW as a cleaning solution

Current research on UPW as a cleaning solution mainly focuses on its use within the semiconductor industry. However there are papers evaluating the cleaning effect when using UPW, stating its potential in other areas and how it might substitute traditional detergents containing surfactants.

According to researchers at ANU (Australian National University), highly degassed UPW may disperse hydrophobic dirt, so called surfactant-free oil-in-water emulsion. The hypothesis behind the phenomena is that gasses within the water and dirt, assist hydrophobic surfaces forming cavitation. Hence, degassed water and dirt will facilitate the dispersion of the hydrophobic particles in the water instead.[17] It has been stated that the degassing of the dirt, in the case of a hydrophobic liquid, resulted in a better cleaning effect compared to degassing the water only.[12], [18] Using a repeating freeze-pump-thaw degassing process along with tough shaking, several hydrophobic natural oils could be dispersed in degassed UPW in the shape of micron-size droplets.[18] Thus, it has been suggested that cleaning potentially can be done without detergents since degassed UPW was demonstrated to be more efficient in cleaning than regular detergents.[19], [12]

As a consequence to the research at ANU, many opinions were uttered within colloidal science. Oil should simply not be soluble in water. The lack of electrostatic or steric stabilizing interactions including a destabilizing interaction due to the hydrophobic effect of water proves this. The hydrophobic effect essentially shows that water molecules will strive to keep as many hydrogen bondings intact as possible when a nonpolar substance is introduced. Hence, water molecules will form a cage-like structure around a hydrophobic substance, all to minimize the contact area with the hydrophobic species. This process is even unfavorable to the system as the order of water will increase, which decreases the system entropy.[19]

Eastoe. J and Ellis. C discusses the production of surfactant-free oil-in-water emulsions, stating how it is achievable yet questioning the ANU theory, saying it is still debatable exactly how these dispersions/emulsions are formed and remain. According to Eastoe and Ellis, the key concept to the surfactant-free oil-in-water emulsions is the repeating freeze-thaw-pump treatment, generating thermal shocks, and not the degassing by itself. Burnett et al. suggest that thermal gradients, from a freeze thaw treatment, produce internal shear forces responsible for the dispersion. However, further research of the surfactant-free oil-in-water emulsion system is still needed to fully determine the physio-chemical mechanism behind its formation and stability.[19]

The ANU studies were picked up by researchers in Linköping, illustrating the technique of removing various types of dirt, such as fingerprints and oil, using UPW only. The UPW used in this study is called Qlean Water (QW) and has successfully been implemented within the manufacturing of printed circuit boards in need of a clean surface prior to lacquering. The QW is said to hold an electric conductivity of 0,03-0,04 µS/cm. Furthermore, QW may be used for washing the front of buildings and hydroelectric dams. However, it is stated that the “cleaning ability” of QW quickly decreases as the conductivity increases and that it vanishes completely once the electrical conductivity reaches 0,05 µS/cm. Thus, the QW has a limited storage time of 24 h before losing its cleaning ability according to the researchers at Linköping.[7] In addition, the mechanism of how QW dissolves dirt is not fully understood and needs further research. Nevertheless, the implementation of QW within the printed circuit board industry has shown positive environmental and economic effects. It was shown to lower emissions of greenhouse gasses yet the exact effect from eliminating chemical detergents is difficult to determine.[7]

Researchers at Malmö University recently compared the cleaning capacity of two types of UPW (MQ water and DIRO® water), tap water, a 10 mM NaCl solution and a 4g/L SDS solution, in terms of removing hydrophobic films from solid surfaces. This cleaning process was investigated using QCM-D technique, where a silica surface was coated with Vaseline. Results showed that both of the purified waters (not degassed) removed > 90% of the Vaseline whilst tap water removed 75% and SDS removed 100%. Additional gravimetric measurements performed also showed that the purified waters (not degassed) removed olive oil from both hydrophilic and hydrophobic surfaces more efficiently than the other cleaning liquids. They suggest that the purified waters achieve such cleaning effects due to their low ionic strength, generating an increased electrostatic repulsion. Charges present on a soil or a surface will strive towards the charge deficient water once in contact. Thus, hydrophobic soils are stabilized in the UPW. The same repulsion is screened in regular tap water (from low levels of inorganic salts present), which is why it shows no such efficiency. Furthermore, UPW is said to assist the roll-up mechanism of cleaning since it showed a higher contact angle than tap water on glass surfaces.[20]

1.5 Further applications of UPW in the cleaning industry

UPW is also used when producing alkaline electrolyzed water, also known as super alkaline ionized water (SAIW)[21] which is said to be another potential cleaning agent. SAIW contains >99% pure water, where the remaining percentage constitute potassium hydroxide (KOH), commonly known as lye. Producing this water requires purification of regular tap water through several filters, including reverse osmosis, essentially obtaining UPW. Secondly, potassium carbonate (K_2CO_3) is added to the purified water as an electrolyte. The water is further subjected to electrolysis, using a specific Japanese technology. The electrolysis splits the water into gasses of oxygen and hydrogen while the K_2CO_3 reacts and forms KOH. The result is an ionized alkaline water with a pH between 12,5-13,1 said to have unique cleaning effects. SAIW is said to solve dirt such as proteins and fats while also being effective against viruses and bacteria.[21][22].Thus, research has been done on UPW as a potential cleaning agent by itself but also as an ingredient when producing SAIW - both potential cleaning agents without surfactants.

1.6 Aim

The aim of this study is to evaluate the cleaning effects of UPW in comparison to SAIW, traditional detergents (with surfactants) and most importantly tap water. Can there be effective cleaning without surfactants and is UPW a significantly better cleaning solution than tap water?

2. Materials and methods

2.1 Literature work

A literature study was conducted at the start of this project to gather information about the process of cleaning, the chemistry behind traditional detergents and their efficiency. Standards for testing detergents aimed for household laundry, industrial laundry and surfaces were gathered as well as current data from previous testing of these, or similar standards. Finally, the characteristics, usage and production of UPW was studied along with further applications of UPW. Current research concerning the effects of water purity when it comes to removing hydrophobic substances from solid surfaces in the absence of surfactants was also studied. The literature study functioned as a foundation for how all experiments would be implemented in this project. In addition, several experienced people within the field of laundry and colloidal science were contacted, where ideas and theories were exchanged.

2.2 Laboratory work

During all laboratory work, tests were done to compare the characteristics and cleaning effects of two types of UPW, SAIW, tap water and one or several surfactant solutions in terms of cleaning textiles and surfaces. MQ water was chosen as one UPW type due to its worldwide recognition and easy availability at KTH. DIRO® water was chosen as the second UPW type since it is a Swedish UPW brand available in the Stockholm region. The soil that was implemented for the cleaning tests were either standardized (from standardized test methods) or chosen according to previous research reports. The different cleaning solutions evaluated in this study can be found in Table 1.

Table 1. Analyzed cleaning solutions and known features.

Cleaning solution	Specifics	Source
UPW-M	MQ water	Milli-Q® IQ 7000 unit at FPT, KTH
UPW-D	DIRO® water	DIRO® unit at Nynäshamns kommun and Brf Förvaltaren
Tap water^{I}	4-6 °dH	FPT lab, KTH
Tap water^{II}	5-6 °dH	Brf Förvaltaren, Solna (or Sundbyberg)
SAIW / ”Z-water”	99,83% UPW 0,17% KOH	PT-Professionals in Karlskrona
SDS	Anionic surfactant	VWR Chemicals
VIA Color Sensitive	Anionic surfactants (5-15%), nonionic surfactants (<5%), enzymes and phosphonate.	Unilever

2.2.1 Water characterization

Water characterization can be done through conductivity measurements. As mentioned in the introduction, conductivity is a good measurement to determine the quality of a water as it is a direct result from the amount of ions within the solution.[8],[9],[10],[11]

2.2.2 Surface cleaning test - QCM-D

Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) was used for surface analysis (surface cleaning tests). The QCM-D is an analysis technique where surface mass changes may be quantified at a nanoscale in real time. These mass changes can be translated into surface interactions and layer formation as molecules either desorb from or adsorb onto the evaluated surface while in air or in a liquid. Furthermore, the dissipation monitoring allows the measuring of energy changes in the system, which in turn can be used to identify the layer properties on the measured surface.[23]

In fact, it is not a direct change in mass (Δm) that is actually measured during the QCM analysis, it is a change in frequency (Δf). The QCM technique is acoustic and based on oscillation where oscillations in the MHz region are detected. The analyzed surface is a quartz crystal disk equipped with two electrodes and coated with the material of interest to be evaluated, eg. silica. Applying an AC voltage allows excitation of the crystal to resonance due to quartz's piezoelectric characteristics. The resonance can in turn be correlated to the crystal thickness, where a change in thickness generates a change in resonance, in the same manner an added mass to the sensing surface will also introduce a change in the resonance frequency. If the viscoelasticity of the sensed material is changing the dissipation will also change. Thus, by following Δf and ΔD as a function of time one can see how much is adsorbed or desorbed from a surface and the dissipation can tell more information on the viscoelastic changes in layer. The schematic figure below (Figure 4) shows the adsorption of molecules onto the analyzed quartz surface along with the resulting change in frequency and dissipation. The shift in frequency can be used to determine the resulting mass change.[23] A decrease in Δf indicates an increased mass.

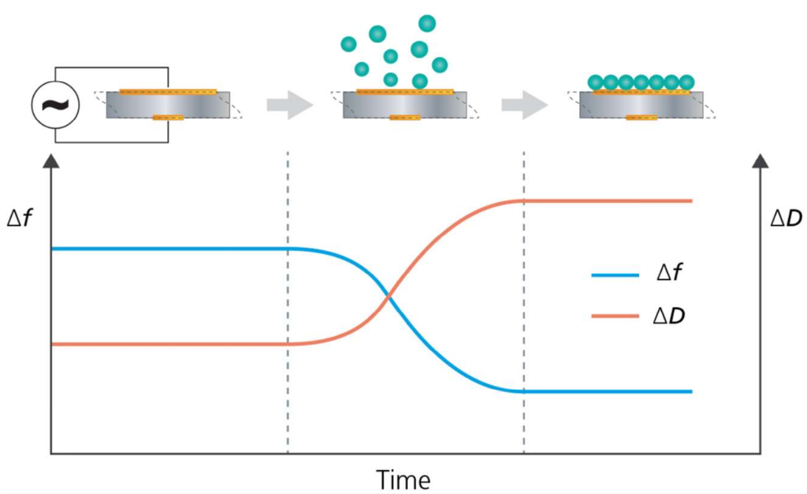

Figure 4. QCM-D measurement of frequency and dissipation as a function of time. (Image adopted from Biolin Scientific webpage)

The Sauerbrey relation, see Equation 1, is what allows the conversion from frequency to mass. Here, *C* is the mass sensitivity constant, based on the properties of quartz sensor while *n* stands for the number of the harmonics used for the analysis.[23]

$$\Delta m = -C \cdot \frac{\Delta f}{n} \qquad (1)$$

The sensitivity constant describes the amount of sensor material (in ng/cm^2) required to establish a frequency shift of 1 Hz. The number of harmonics, *n*, represents the overtone number of the frequencies for the specific crystal. The lowest resonance frequency is known as the fundamental frequency (*n*=1), while additional resonance frequencies are overtones (*n*=3,5,7 etc). During analysis, each resonance frequency will provide specific information about the studied system.[23]

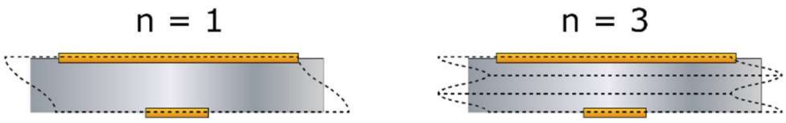

Figure 5. Cross section of analyzed quartz crystals resonating at the fundamental frequency, n=1(left) and the third overtone, n=3 (right). (Image adopted from Biolin Scientific webpage)

2.2.3 Laundry tests

Laundry tests were performed with inspiration taken from the European standard, *EN 60456:2016*; *Clothes washing machines for household use – Methods for measuring the performance.* While this standard is established to evaluate the performance of washing machines[24], it is, as far as research done in this thesis, the best alternative to evaluating the washing performance of a cleaning agent in Sweden today.

The laundry tests are performed in terms of washings (full washing programs) in washing machines loaded with soiled textiles. The soil applied within *EN 60456:2016* and within this project, are standardized cotton “stain stripes” from Swissatest (Figure 6). The “stain squares” represent the following soils; white (unsoiled), sebum, carbon/soot (mixture of carbon black and mineral oil), blood, chocolate, and wine. These soils are specifically selected and applied to determine different washing characteristics, which can be seen in table 2. [24]

Table 2. Evaluated cleaning characteristics[24].

Soil	Washing effect
sebum	*Scouring effect* (mainly due to mechanical and thermal action)
soot	*Scouring effect* (mainly due to mechanical and thermal action)
blood	*Removal of protein pigments*
chocolate	*Removal of organic pigments*
wine	*Bleaching effect*

The stain stripes are to be washed when attached to a cotton towel. For each wash, 4 towels with stain strips are added. The same type of cotton towels, without strips, are used as filling material to obtain a specific washing load. The stain strips and clean cotton towels are loaded according to the description in the *EN 60 456:2016*.[24]

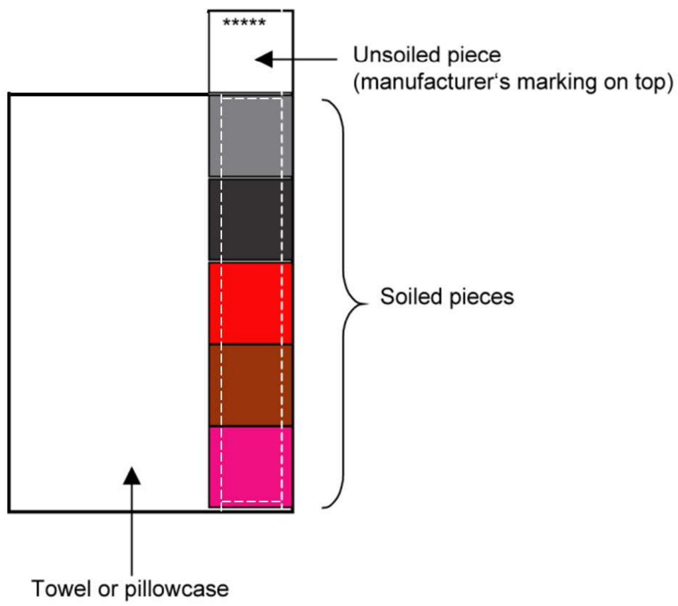

Figure 6. Cotton towel/pillowcase with an attached stain strip showing the 5 different standardized soils.[24]

The washing performance is evaluated through comparing the reflectance of each stain strip before and after wash. The reflectance data before wash is provided by the stain strip manufacturer, Swissatest.[24] Reflectance of each soil square after wash is measured using a similar spectrophotometer as used by Swissatest. A ratio (q) is calculated using the average reflectance of each soil after wash (C_{test}) and the average reflectance of each soil before wash (C_{ref}). See Equation 2, the higher q value, the better cleaning effect. If $q > 1$ some soil has been removed while a $q = 1$ means no change of the soil.

$$q = \frac{C_{test}}{C_{ref}} \tag{2}$$

2.3.4 Emulsion test

Emulsion tests were performed to evaluate the dispersion/separation process of each cleaning solution and a hydrophobic liquid.

2.3.5 Cleaning test of individual fibers followed by optical microscopy

Cleaning performance followed by optical microscopy were conducted on individual fibers to visualize the cleaning process of a fiber, partly covered in a hydrophobic soil, on a microscopic level in real time.

3. Experimental

3.1 Water characterization

Water as well as surfactant solutions were measured in terms of conductivity. The conductivity of each cleaning solution was measured at least five times* distributed during a period of two months, using a conductivity meter (Thermo Scientific). After measurements, an average value was calculated for each cleaning solution. *DIRO® water stored in plastic DIRO® bottles (see Appendix 9.8; Figure 42) was only measured three times distributed during a period of 2 months, due to a drastic change in conductivity (See Figure 10).

3.2 Surface cleaning test

Surface cleaning tests were performed with QCM-D-analysis. The "soil" was added through spin coating Vaseline onto the surface of the quartz crystals (QSX 303 SiO2, Biolin Scientific). Cleaning solutions to be analyzed using QCM-D can be found in Table 3.

Table 3. Analyzed cleaning solutions and known features.

Cleaning solution	Specifics	Source
UPW-D	DIRO® water	SWATAB-unit at Brf Förvaltaren
SAIW / "Z-water"	99,83% UPW 0,17% KOH	PT-Professionals, Karlskrona
Tap water[I]	4-6 °dH	FPT lab, KTH
SDS	Anionic surfactant	VWR Chemicals

3.2.1 QCM-D

3.2.1.1 Analysis - Bare crystals

Before all measurements, the QCM chambers parts that will get in contact with either the test liquids (metall, o-ring and rubber sealing), were soaked in a 2-4% Deconex solution for at least 30 minutes. After this, the parts were rinsed extensively with MQ water and stored in a glass beaker with MQ water until drying in a flow of N_2 gas and mounting just prior the start of the measurements. Before each measurement, the chamber was rinsed with MQ water and dried with N_2 gas. The o-ring and rubber sealing was also soaked in a 2-4% -Deconex solution for at least 30 min, rinsed several times and stored dry. Before each measurement, the o-ring and rubber sealing was rinsed with MQ water and dried with N_2 gas. Prior to analysis, each crystal was rinsed with water-ethanol-water, dried with N_2 gas and further cleaned in a UV ozone cleaner for at least 20 minutes.

Starting measurements were done with dry bare quartz crystals (QSX 303 SiO2, Biolin Scientific) in air and MQ water only to evaluate the absolute frequency and dissipation standard deviation of the QCM-D analysis. According to A. Tsompou and V. Kocherbitov the main source of errors is mounting the analyzed crystal back and forth into the QCM measuring chamber. This action results in an error of ± 20 Hz in resonance frequency.[20] To test this, five different quartz crystals were measured in air 20 times and MQ water 10 times generating a total number of 100 measurements/crystal in air and 50 measurements/crystal in MQ water. The liquid flow rate was set to 0,100 ml/min during MQ measurements.

3.2.1.2 Analysis - Vaseline coated crystals

Before coating, each quartz crystal was rinsed with MQ water/ethanol/MQ water before additional cleaning in a UV Ozone cleaner for 10 minutes. This cleaning procedure was repeated two times.

The Vaseline (Carl Roth) was diluted 12 times in Toluene and spin coated onto the crystals at 1200 rpm for 30 seconds. 100 µl Vaseline solution was used for each crystal to establish a layer thickness of about 500 nm. After coating, each crystal was dried in a fume hood for at least 30 minutes.

According to A. Tsompou and V. Kocherbitov[20] the optimal coating thickness when evaluating a washing procedure should be between 20 and 100 nm. However, the suggested coating thickness was tested and it was observed that the whole Vaseline layer disappeared once Vaseline coated silica surface (with the suggested thickness of the coating) was dipped in water, directly when entering the air water interface. Hence, it was decided to evaluate the cleaning procedure using a thicker Vaseline layer in the present study.

The Vaseline coated crystals were used to measure the absolute frequency and dissipation in the following cleaning agents; Milli-Q® water, DIRO® water, Z-water, tap water[I] and a 4 g/L SDS-solution. The liquid flow rate was set to 0,250 ml/min. All measurements were conducted using the following protocol;

→ Absolute dissipation and frequency was measured for a bare crystal in air 5 times - the 5th measurement was set to run for 10 minutes.

→ The bare crystal was spin coated with 100 µl of the Vaseline solution and dried for 30 minutes. Then, the absolute dissipation and frequency was measured for the coated crystal 5 times in air where the 5th measurement was set to run for 10 minutes.

→The liquid (cleaning agent) was introduced and pumped through the system at 0,250 ml/min for 40 minutes, where the absolute frequency and dissipation was measured.

→ The crystal was taken out and blow dried carefully with N_2 gas, together with drying of the chamber. Again, the absolute dissipation and frequency was measured for the dried crystal 5 times in air where the 5th measurement was set to run for 10 minutes. All QCM data calculations were done using QTools and Microsoft Excel.

Between each measurement set, the liquid tubes and chamber were cleaned. The analyzed crystal was replaced with a “cleaning” crystal and the following cleaning scheme was performed using a 0,3 ml/min flow:

→10 min of Deconex solution (10%) followed by a 10 min rinsing with Milli-Q® water

→10 min of HCl solution (0,1 M) followed by a 10 min rinsing with Milli-Q® water.

The chamber was stored in a 10% Deconex solution and the o-ring and rubber sealing was rinsed in a 10% Deconex solution, dried with N_2 gas and stored dried, until the next measurement.

3.3 Laundry tests

From *EN 60456:2016* it was recommended and therefore decided to perform three washings (full washing programs) per each cleaning solution tested, in both 40 ℃ and 60 ℃, respectively. This resulted in a total number of six washings per cleaning agent. However, due to a lack of standard soil material only one washing per temperature could be done with SAIW.

3.3.1 Towel preparation

New cotton towels (Westford Mill tea towel, 100% cotton) were used as filling material to obtain the right washing load for the tests. To avoid any potential chemicals left from production, all towels were washed at 45 minutes with "VIA Color Sensitive" at 40 degrees followed 3 times 45 minutes at 40 degrees with just tap water - to wash away any surfactants left from the initial first wash. The laundry machine used for preparation was Electrolux CompassPro (Figure 7) and the program used for all preparation washes was called "Normal 40". For the initial first wash, ½ dl VIA Color Sensitive was added for pre wash, and the same amount for the main washing cycle. The "Normal 40" program lasted for 45-50 min. Post wash, all towels were dried for 50 minutes in a Electrolux Wascator (T3190) drier.

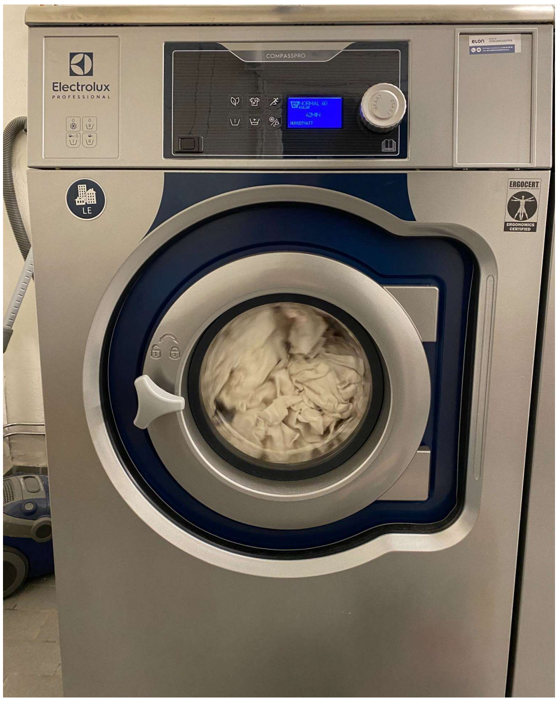

Figure 7. Cotton towels being washed to avoid any potential chemicals left from production.

3.3.2 Stain strip preparation

The Swissatest standardized "stain strips" were sewed onto cotton towels using a sewing machine. Each stain strip was attached to one individual towel according to Figure 6.

3.3.3 Washing procedure

Laundry tests were done with inspiration taken from the European standard, *EN 60456:2016*; *Clothes washing machines for household use – Methods for measuring the performance*. Cleaning solutions included in the laundry tests can be found in Table 4.

Table 4. Analyzed cleaning solutions and features.

Cleaning solution	Specifics	Source
UPW-D	"DIRO® water"	SWATAB-unit at Brf Förvaltaren
SAIW / "Z-water"	99,83% UPW, 0,17% KOH	PT-Professionals, Karlskrona
Tap water[II]	5-6 °dH	Förvaltaren Brf, Sundbyberg
VIA Color Sensitive	Anionic surfactants (5-15%), nonionic surfactants (<5%), enzymes and phosphonate.	Unilever

The machines used for washing tests with DIRO®, tap water[II] and VIA Color Sensitive were Electrolux W465H. The machine used for Z-water was a PODAB ProLine Hx 65. Before each test, all machines were run empty at "Normal 40" for at least 5 minutes to avoid any potential leftovers from earlier washes. See measurement specifics of all cleaning agents in Table 5

Table 5. Measurement specifics for DIRO®, tap water[II] and VIA (column 1) together with Z-water (column 2).

Machine	Electrolux W465H (7 kg)	PODAB ProLine 65 HX (8 kg)
Washing load (kg)	Half ≈ 3,5	Half ≈ 4
Stain strip load (g)	20 x 4	20 x 4 (40°C) resp.20 x 3 (60°C)
Mass/towel (g)	59,5	59,5
Total number of towels (no.)	54	62
Total towel load (kg)	3,213	3,689
Total test load (kg)	3,293	3,769 (40°C) resp 3749 (60°C)

Figure 8. Loading procedure, showing folded filling material (cotton towels) with a stain strip on top.

3.3.3.1 DIRO® water and tap water[II]

DIRO® water and tap water[II] were run in the same machines, programmed according to the DIRO® system. For further information regarding the washing program see Appendix 9.6.

Table 6. Laundry measurement data for DIRO® and tap water[II].

Cleaning solution	*DIRO®*		*Tap water[II]*	
Washing program	"Normal 40" *DIRO® system*	"Normal 60" *DIRO® system*	"Normal 40" *DIRO® system*	"Normal 60" *DIRO® system*
Energy consumption (kWh)	N/A	0,32	N/A	0,32
Water consumption (l)	N/A	66	N/A	66
Temperature (℃)	40	60	40	60
Duration (min)	50	63	50	63
Washings (no.)	3	3	3	3
Stain strips/ wash (no.)	4	4	4	4

3.3.3.2 VIA Color Sensitive

VIA Color Sensitive washings were done in Electrolux W465H as DIRO® - and tap water[II], but with the standard washing programs optimized for detergents. No further information regarding the washing program could be collected due to secrecy by Electrolux Professionals.

Table 7. Laundry measurement data for VIA Color Sensitive.

Cleaning solution	*VIA Color Sensitive*	
Detergent load	0,5 dl pre wash and 1 dl main wash	
Temperature (℃)	40	60
Program	*"Normal 40"*	*"Normal 60"*
Energy consumption (kWh)	N/A	0,15
Water consumption (l)	N/A	66
Duration (min)	40-49	49
Washings (no.)	3	3
Stain strips/wash (no.)	4	4

3.3.3.3 Z-water

Due to a lack of material only 1 washing per temperature could be done with SAIW/ Z-water. For further information regarding the washing program see Appendix 9.8.

Table 8. Laundry measurement data for Z-water.

Cleaning solution	*SAIW/ Z-water*	
Washing program	"Normal 40" *Z-water*	"Normal 60" *Z-water*
Energy consumption (kWh)	N/A	N/A
Temperature (℃)	40	60
Duration (min)	41	49
Washings (no.)	1	1
Stain strips/wash (no.)	4	3

3.3.3 Analysis

Reflectance measurements of all stain strips after a wash was performed using a Minolta spectrophotometer CM-3610d. Each "soil square" was measured at four different positions. Thus, an average reflectance of each soil could be calculated for each cleaning solution and washing temperature. The statistical calculations were done using Microsoft Excel, see Appendix 9.2. The same reflectance values for all stain strips before wash was collected from the manufacturer (Swissatest). The q value was calculated using (C_{test}) and (C_{ref}). Finally, the q value of each cleaning solution and temperature were compared.

3.4 Emulsion test

Emulsion tests were performed using the setup pictured in Figure 9. 15 ml of each cleaning solution (Table 9) were mixed with 2,5 ml rapeseed oil in glass graded formulation test tubes. Each tube was manually shaken vigorously for 15 seconds before evaluation of dispersion/separation. All test tubes were filmed for 35 minutes to easier evaluate the separation process over time.

Table 9. Cleaning solutions tested in emulsion test.

Cleaning solution	Specifics	Source
UPW-M	MQ water	Milli-Q® IQ 7000 unit at KTH
UPW-D	DIRO® water	SWATAB-unit at Brf Förvaltaren
SAIW / “Z-water”	99,83% UPW, 0,17% KOH	PT-Professionals, Karlskrona
Tap water[I]	4-6 °dH	FPT lab, KTH
SDS	Anionic surfactant	VWR Chemicals
VIA Color Sensitive	Anionic surfactants (5-15%), nonionic surfactants (<5%), enzymes and phosphonate.	Unilever

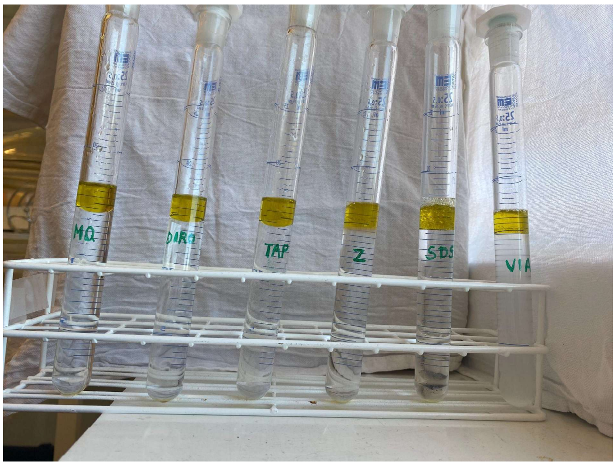

Figure 9. Emulsion test setup, showing each cleaning solution and oil before mixing (shaking).

3.5 Cleaning test of individual fibers followed by optical microscopy

Cleaning tests were conducted on single fibers using a microscope (DINO-lite Premier Digital Microscope, AM7013MZT) to imaging the cleaning process. A lyocell fiber (or cotton filament), partly covered with olive oil, was imaged in air and during immersion in the cleaning liquid. The fibers were further flushed with the cleaning solution and the "cleaning process" could be imaged in real time. See Figure 10 for the experimental setup.

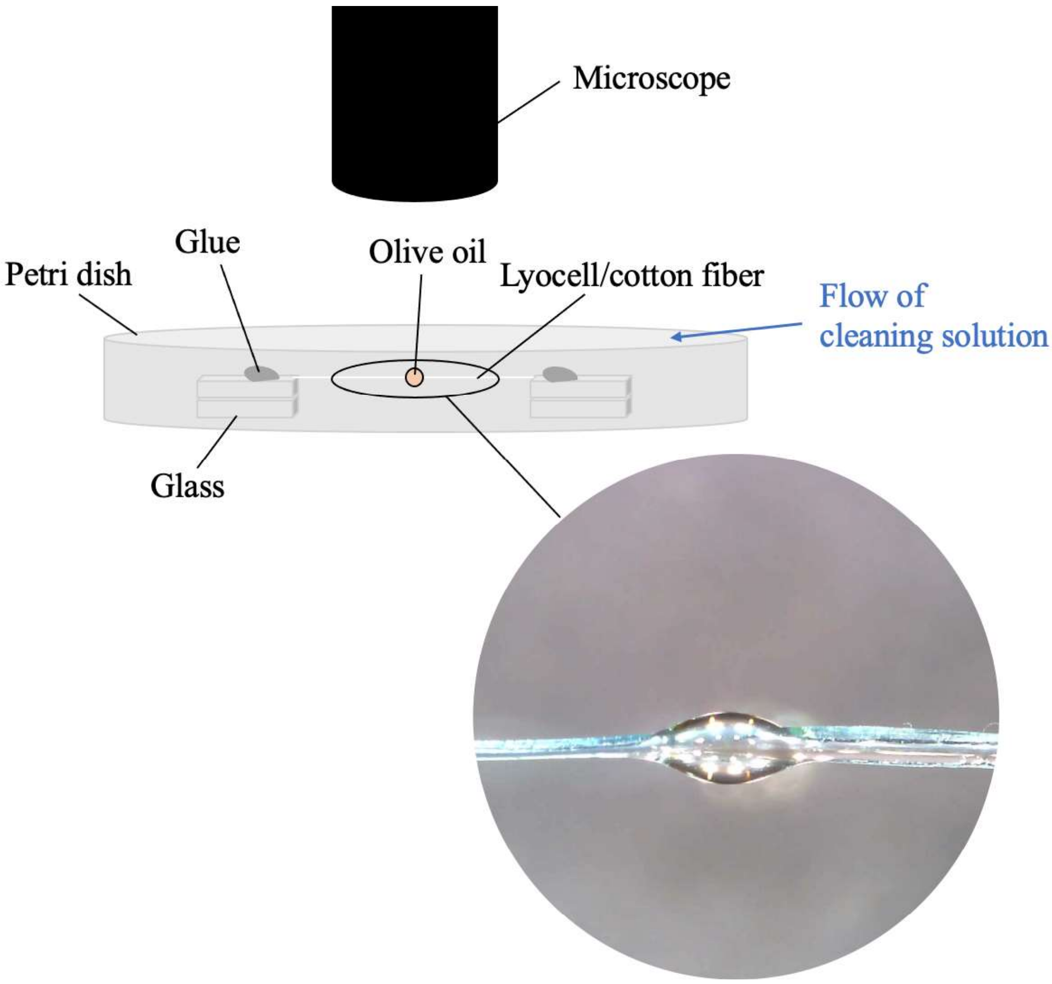

Figure 10. Experimental setup for cleaning tests of individual fibers followed by optical microscopy

4. Results

4.1 Water characterization

Table 10. Conductivity data for all cleaning solutions.

Cleaning solution	Specifics	Source	Conductivity (µS/cm)	Temperature (℃)
UPW-M	MQ water	Milli-Q unit at KTH	0,508	23,0
UPW-D	DIRO® water (plastic bottle)*	SWATAB-unit Nynäshamn	See Fig 10.	-
UPW-D	DIRO® water (glass bottle)	SWATAB-unit Brf Förvaltaren	0,665	21,5
SAIW / "Z-water"	99,83% UPW 0,17% KOH	PT-Professionals Karlskrona	8,23	22,5
Tap water[I]	4-6 °dH	FPT lab, KTH	280	22,9
Tap water[II]	5-6 °dH	Brf Förvaltaren	289	20,9
SDS	4 g/L SDS in tap water[I]	VWR Chemicals	858	22,8

*DIRO® water was stored in both glass and plastic DIRO® bottles (see Appendix 9.8; Figure 42). The DIRO® water stored in plastic bottles changed drastically in conductivity in less than a month which is why a specific conductivity could not be determined for this water. Instead, a conductivity change over time was generated, (Figure 11). A line was inserted in this graph to visualize the change to readers. All other cleaning solutions showed a consistent conductivity over time and so an average conductivity could be calculated.

Figure 11. Conductivity measurement of DIRO® water stored in a plastic DIRO® bottle.

4.2 Surface cleaning test

4.2.1 QCM-D

4.2.1.1 Bare crystals

Statistics calculated using frequency data of each overtone extracted from 50 measurements of bare clean crystals in air, repeated twice together with 50 measurements of bare crystal in MQ water. The fundamental overtone (*n* = 1) was left out due to a large inconsistency that is common for this overtone for this instrument.

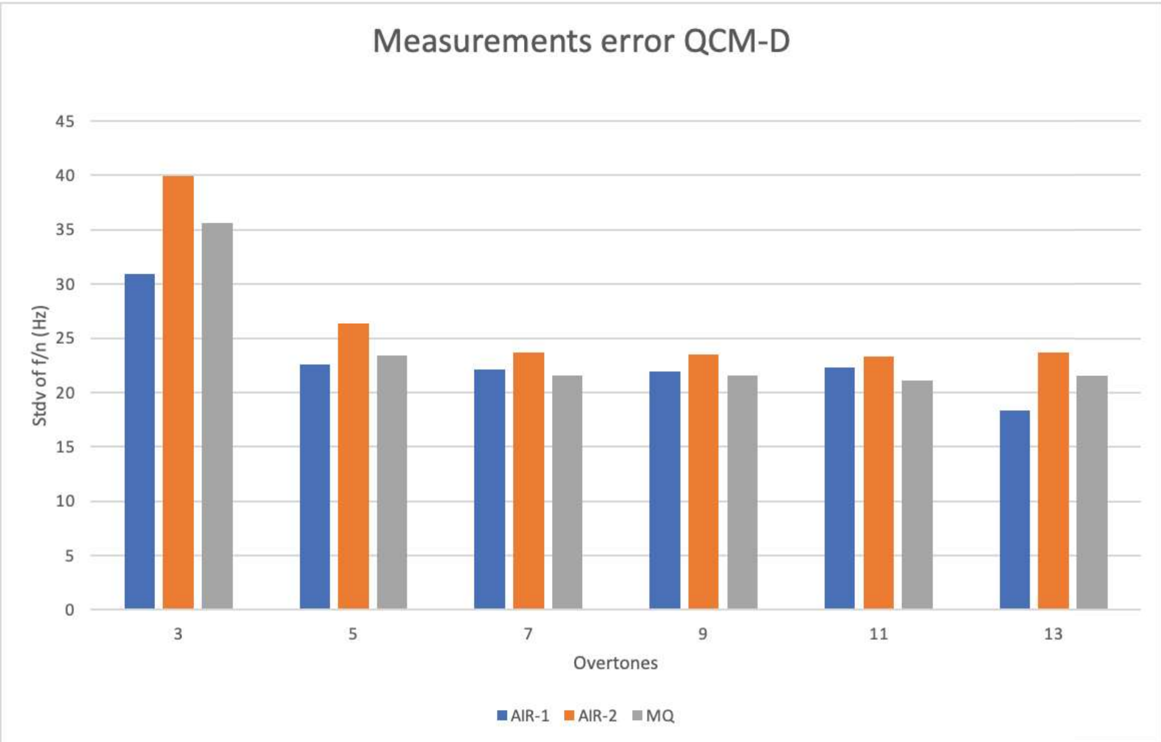

Figure 12. Measurement error of each overtone while measuring a bare crystal in air, repeated twice in air and one time in MQ water, the y-axis corresponds to the calculated standard deviation of the normalized frequency in (Hz) over 10 measurements in air and 5 measurements in MQ water.

The frequency shift of a crystal going from air to MQ water was measured for five different bare and clean crystals. Each crystal was tested five times to determine the standard deviation of the shift. The normalized frequency shift (Δf/n) for the different crystals for all measured overtones are presented in Figure 13. Again, the fundamental frequency (*n* = 1) was left out due to a large inconsistency.

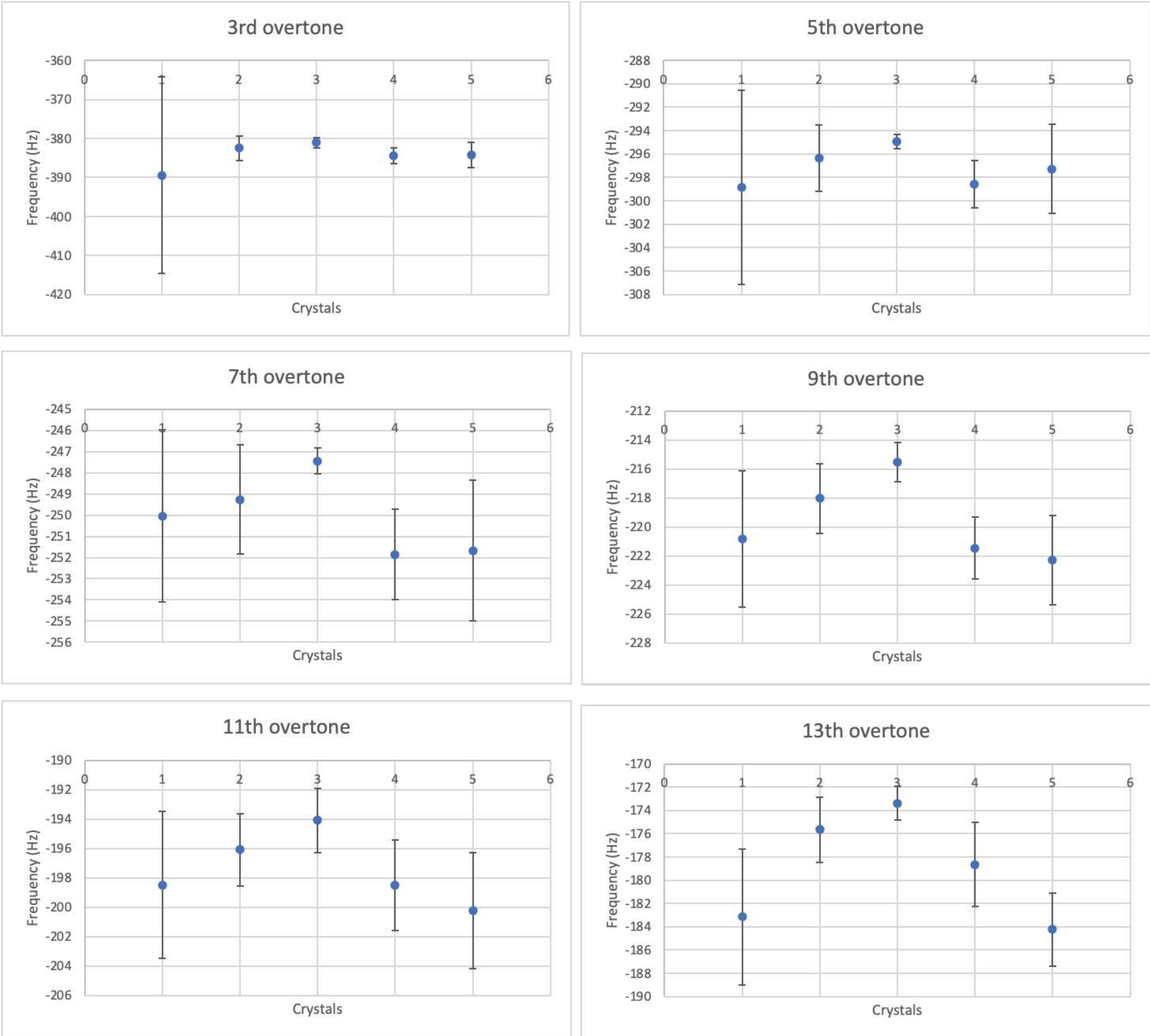

Figure 13. Sub plots for each individual overtone (except n=1) showing the frequency shifts, Δf/n (y-axis) from air to MQ water for all 5 crystals measured (x-axis).

4.2.1.2 Coated crystals

The measured frequency shift (*n=3)* of a bare crystal going through coating and washing can be seen in Figure 14. The 3rd overtone was chosen because it showed the highest consistency during all measurements. As can be seen in Figure 13, a bare crystal was first measured in air as reference and zero level. Using the frequency shift from bare crystal to coated crystal it is possible to calculate the layer thickness of the spin-coated Vaseline layer. Thus, it is possible to see through the different frequency shifts, that the different crystals received different coating thicknesses even though they were treated the exact same way. Individual plots for each cleaning solution can be found in Appendix 9.1; Figure 27-31.

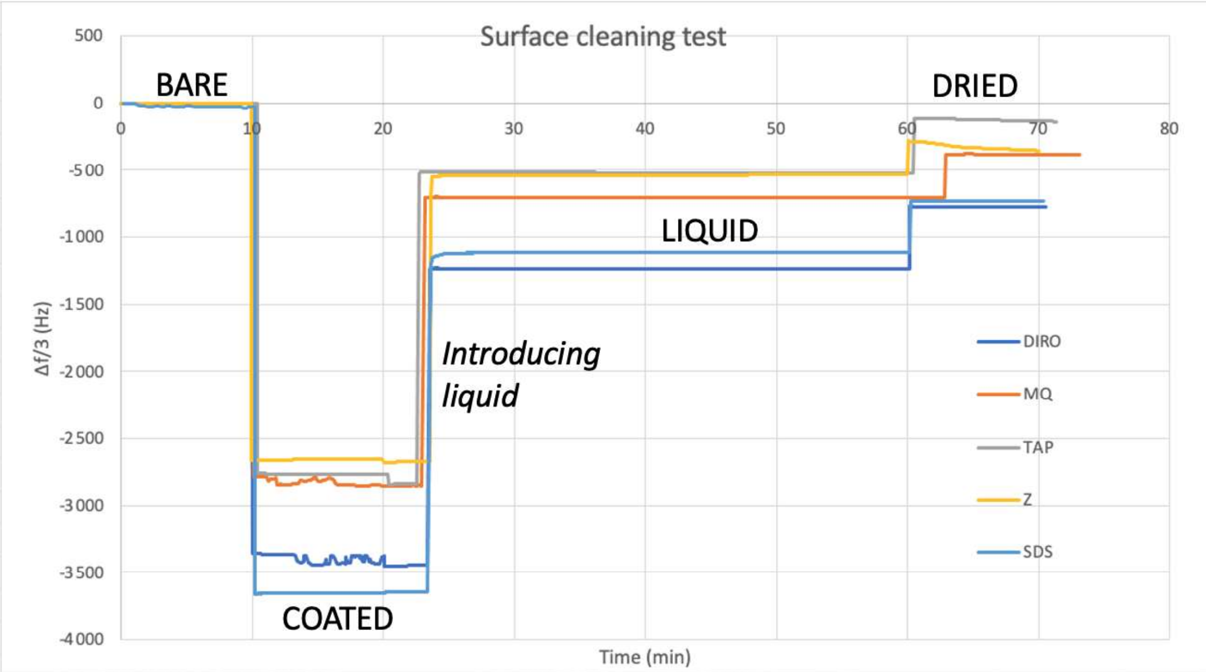

Figure 14. QCM data for each surface cleaning test, showing Δf/3 as a function of time as the crystal went from bare to coated, introduced to a liquid (cleaning agent) and finally dried.

The surface cleaning test performance was calculated in percentage as all coated layers behaved differently (received different thicknesses) and is given in Table 11. Thus, the performance result is a direct measurement of the coating thickness at the start compared to the coating thickness when the crystal was finally dried after wash.

Table 11. Calculated surface cleaning test performance of each cleaning solution.

Cleaning solution	MQ water	DIRO® water	Z-water	Tap water[I]	SDS
Performance (%)	86,5	77,3	87,5	95,5	80,5

4.3 Laundry tests

4.3.1 Laundry results, 40 ℃

The statistical calculation of each reflectance ratio can be found in Appendix 9.2.
The reflectance ratio data of a reference detergent was also included in the analysis below. This data was provided by the stain strip manufacturer, Swissatest. Unfortunately no further information, including type of detergent, machine or time could be given for this cleaning solution.

Table 12. Calculated reflectance ratio, q (without standard deviation) of each cleaning solution.

Soil reflectance ratio (*q*)	DIRO®	Tap[II]	Z-water	Via Color Sensitive	Reference detergent
sebum	1,25	1,21	1,23	1,26	1,44
soot	1,55	1,41	1,39	1,45	1,93
blood	2,34	2,39	1,78	4,80	4,84
cocoa	1,22	1,23	1,14	1,60	1,71
wine	1,48	1,40	1,35	1,21	1,49

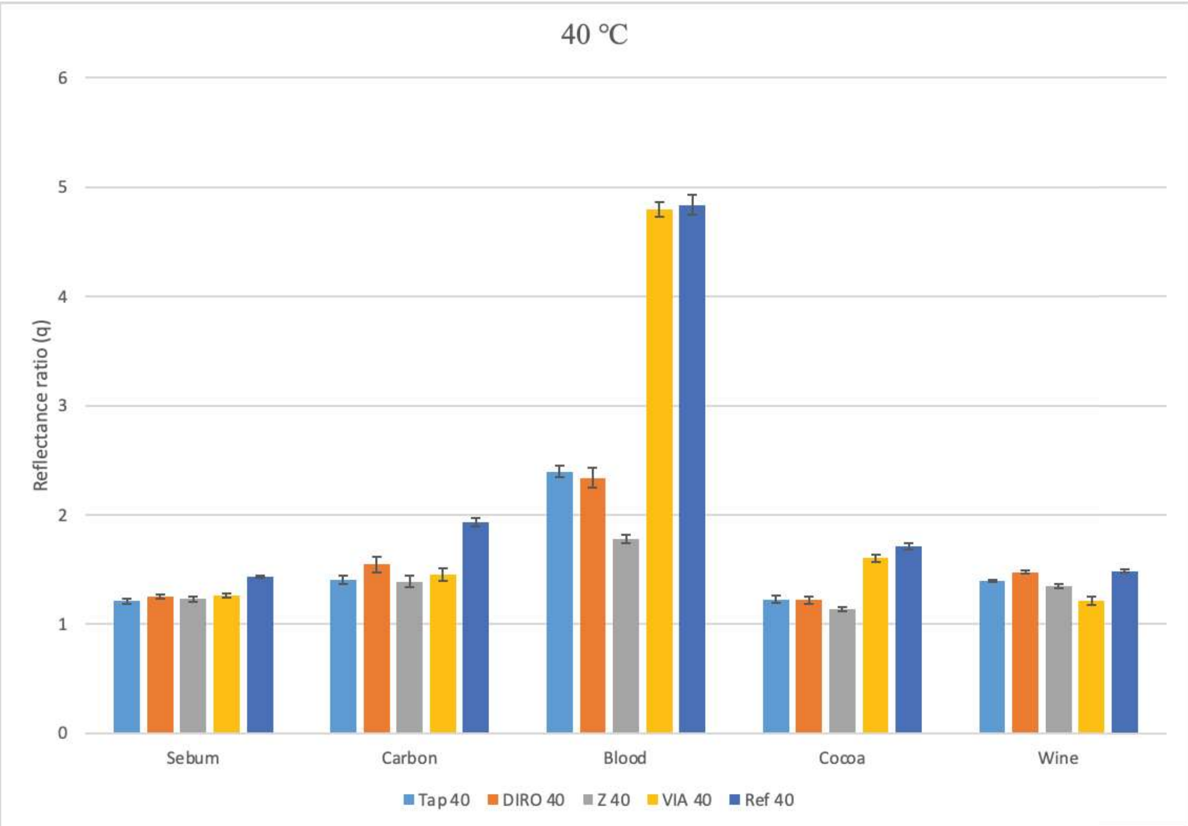

Figure 15. Reflectance ratio (q) of soil reflectance before and after wash at 40℃ for all analyzed cleaning solutions and a reference detergent, including standard deviations.

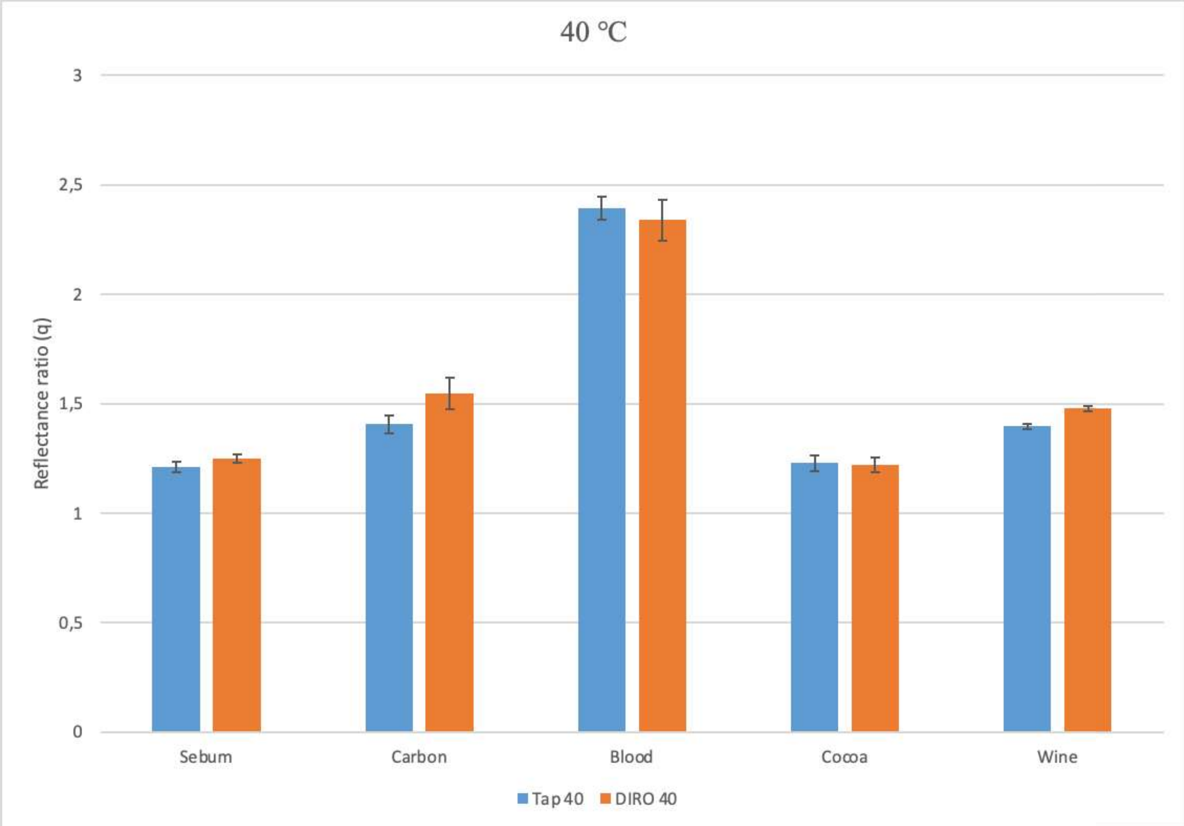

Figure 16. Reflectance ratio (q) of soil reflectance before and after wash at 40℃ for tap water[I] and DIRO® for all individual soils, including standard deviations.

From Figure 15 it can be seen that the reference detergent was the most effective cleaning solution for all stains. Furthermore, in Figure 16 there seems to be a significant difference in performance between DIRO® and tap water[II] for carbon and wine where DIRO® performed slightly better than tap water. However, it is important to enable an overall comparison of the performance between all laundry results from the different cleaning solutions. To make this comparison, an overall average of the ratios of the five different stains for each cleaning solution were calculated. The overall averages are summarized in Figure 17. Looking at the overall results, there is no significant difference in performance between DIRO® and tap water[II] or Z-water (see Figure 17). In addition, there was a significant difference where VIA Color Sensitive and the Reference detergent overall performed better compared to DIRO®, tap water[II] and Z-water.

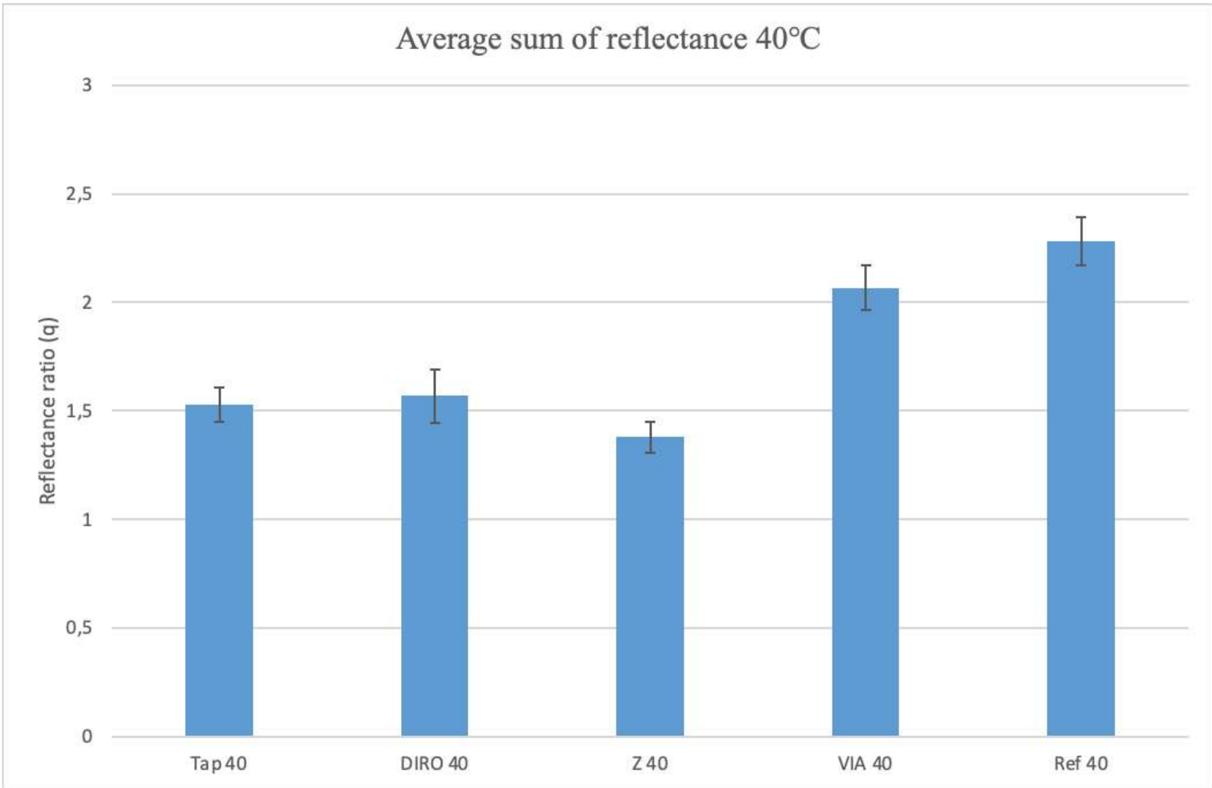

Figure 17. Average sum of reflectance ratio (q) for each cleaning solution at 40℃, including standard deviations.

4.3.2 Laundry results, 60 ℃

See Appendix 9.2 for statistical calculations. Again, reflectance data of a reference detergent, provided by Swissatest, was included in the analysis. Unfortunately no further information, including type of detergent, machine or time could be given.

Table 13. Calculated reflectance ration (without st dev) of cleaning solution.

Soil reflectance	DIRO®	Tap^II	Z-water	Via Color Sensitive	Reference detergent
sebum	1,33	1,23	1,24	1,26	1,52
soot	1,65	1,45	1,55	1,75	2,13
blood	2,44	2,44	1,77	4,59	5,14
cocoa	1,25	1,26	1,20	1,63	1,93
wine	1,57	1,44	1,42	1,23	1,72

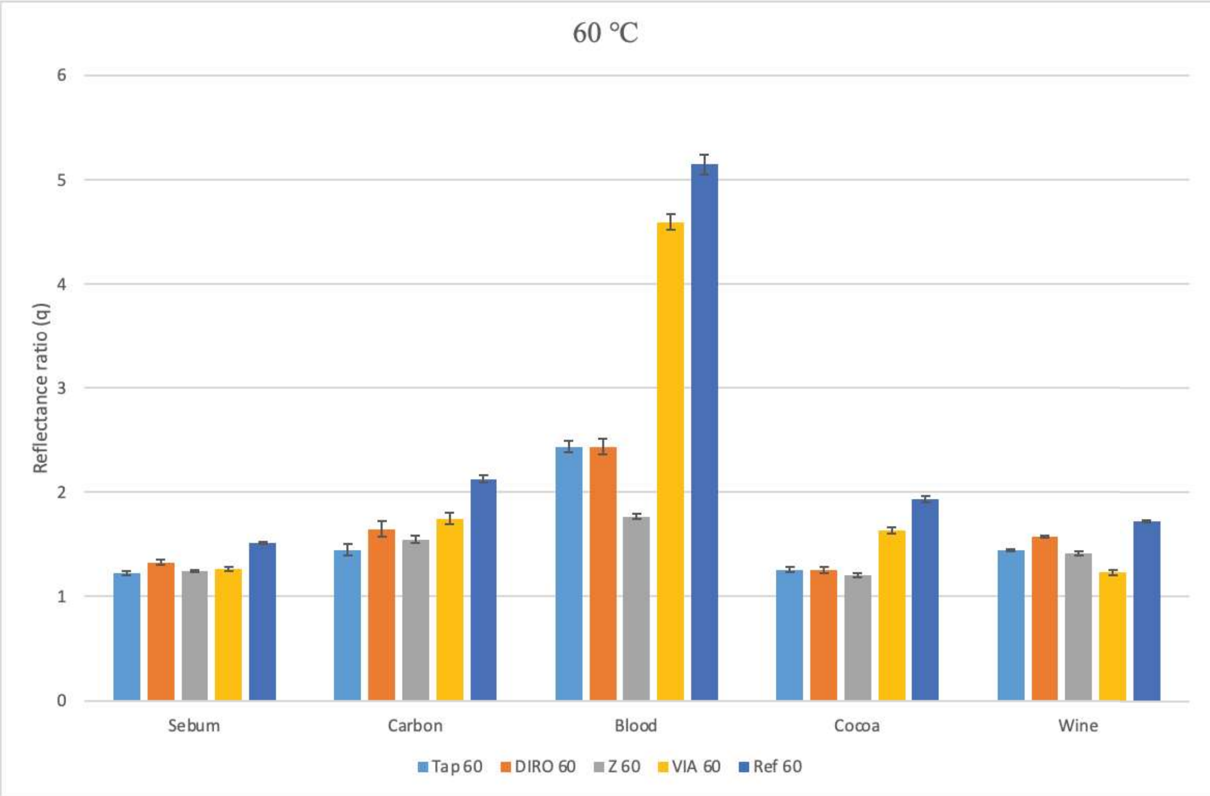

Figure 18. Reflectance ratio (q) of soil reflectance before and after wash at 60℃ for all analyzed cleaning solutions and a reference detergent for all individual soils, including standard deviations.

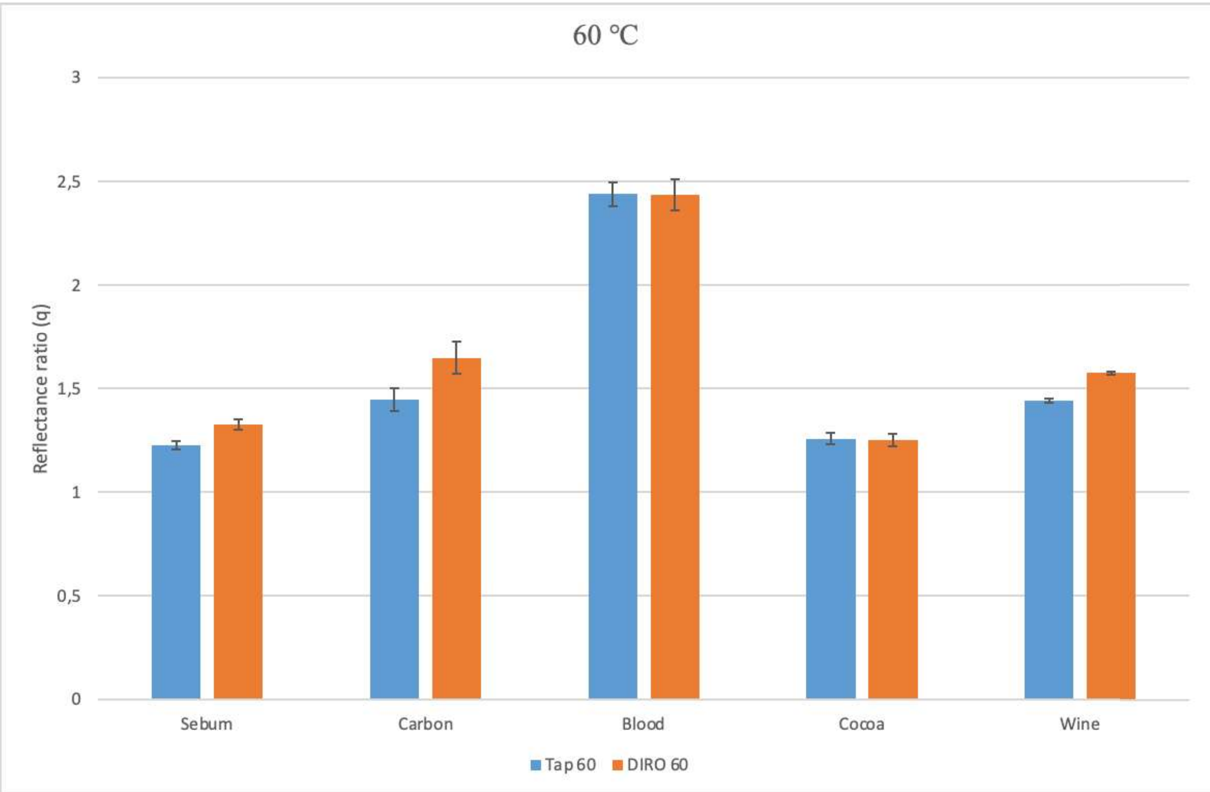

Figure 19. Reflectance ratio (q) of soil reflectance before and after wash at 60℃ for tap water and DIRO® for all individual soils, including standard deviations.

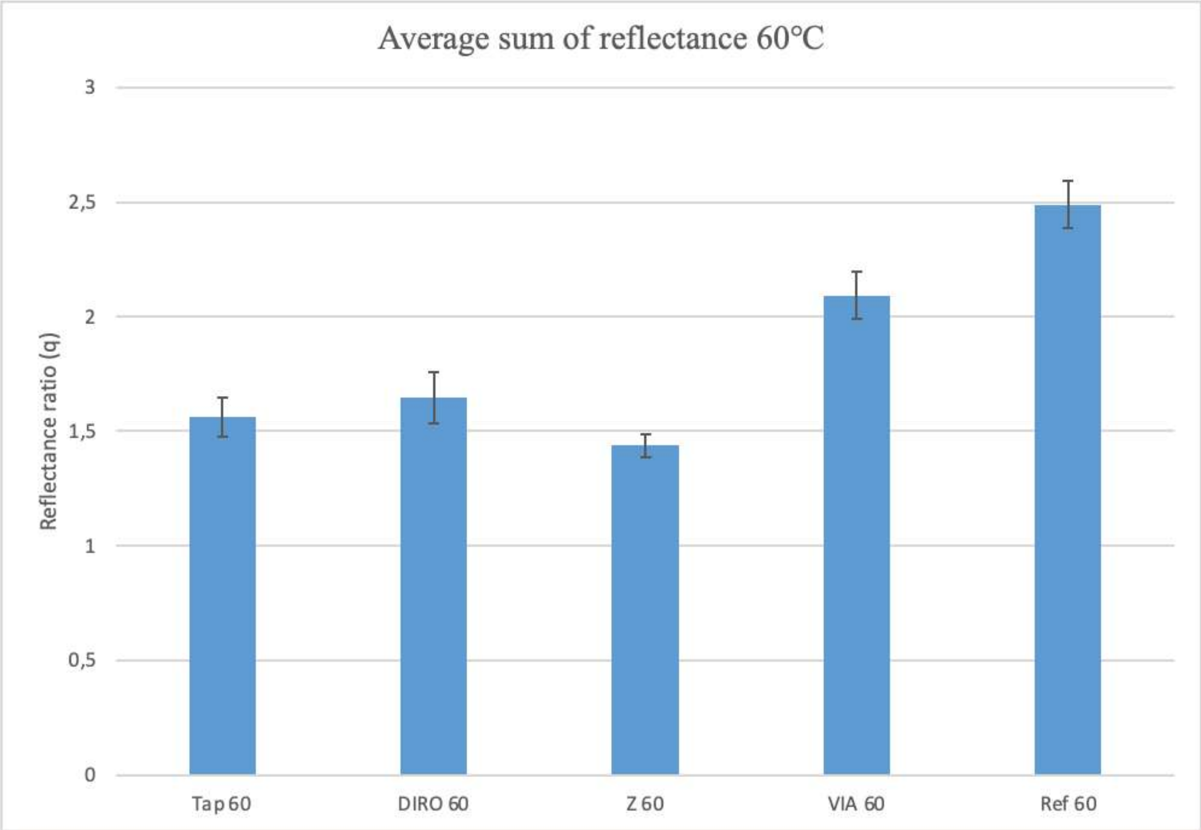

Figure 20. Average sum of reflectance ratio (q) for each cleaning solution at 60℃, including standard deviations.

Again, it can be found that the reference detergent was the most effective cleaning solution for all stains. There seems to be a significant difference in performance for DIRO® and tap water[II] in sebum, carbon and wine. However, overall there was no significant difference in performance between DIRO® and tap water[II] (see Figure 20). In addition, there was a significant difference in performance for DIRO®, tap water[II] and Z-water in comparison to VIA Color Sensitive and the Reference detergent. Finally, DIRO® was significantly higher in overall performance in comparison to Z-water but not compared to tap water[II].

4.4 Emulsion test

The emulsion test was performed during a period of 35 minutes.

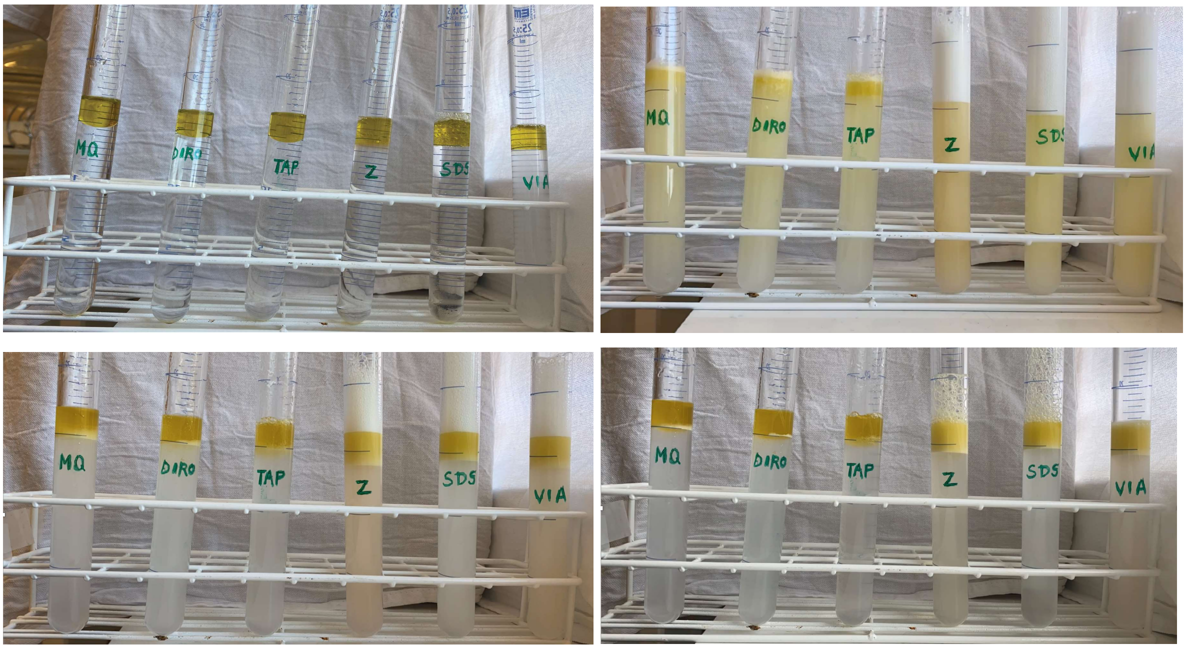

Figure 21. Emulsion test setup showing the separation of cleaning solutions and oil before mixing/shaking (upper left), after 3 seconds (upper right), after 3,5 minutes (lower left) and after 35 minutes (lower right).

4.4 Cleaning test of individual fibers followed by optical microscopy

The cleaning tests on individual fibers were filmed which is why only individual images could be inserted in this report. All images show the fiber from start, a fiber in air partly covered in olive oil droplets. Additional images show when the cleaning liquid “hits” the olive oil droplets and further events when the fiber is soaked in the cleaning solution.

4.4.1 Olive oil - DIRO® water

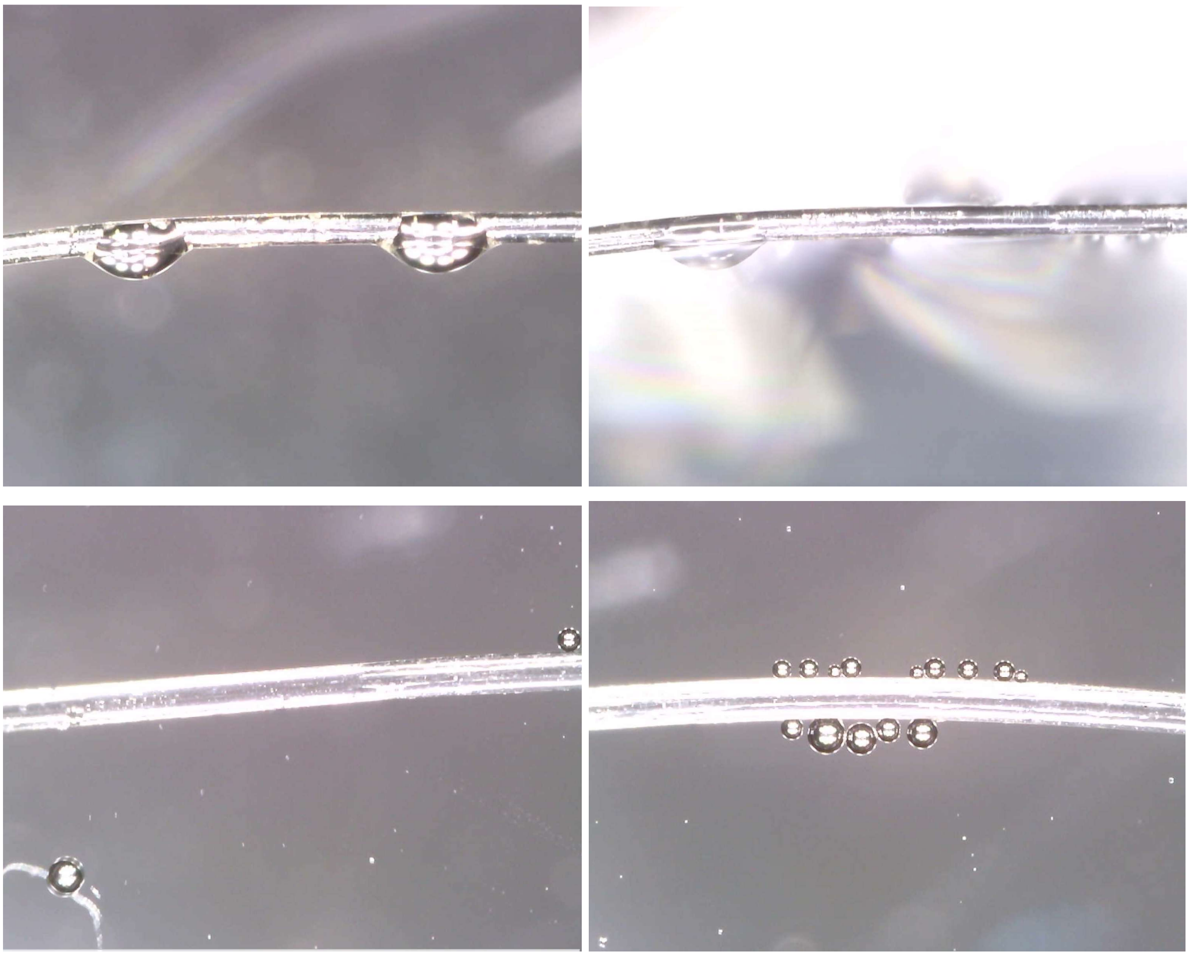

Figure 22. Microscopy images of a lyocell fiber in air, stained with drops of olive oil (upper left), the same fiber in DIRO® water (upper right and lower left) again the same fiber in DIRO® water a couple seconds later (lower right).

From these pictures it can be seen that the DIRO® water hits and washes over the olive oil droplet quickly. However, there is still olive oil left on the lyocell fiber surface and small olive oil drops make their way back and redeposit on the fiber surface after a few seconds.

4.4.2 Olive oil - VIA Color Sensitive

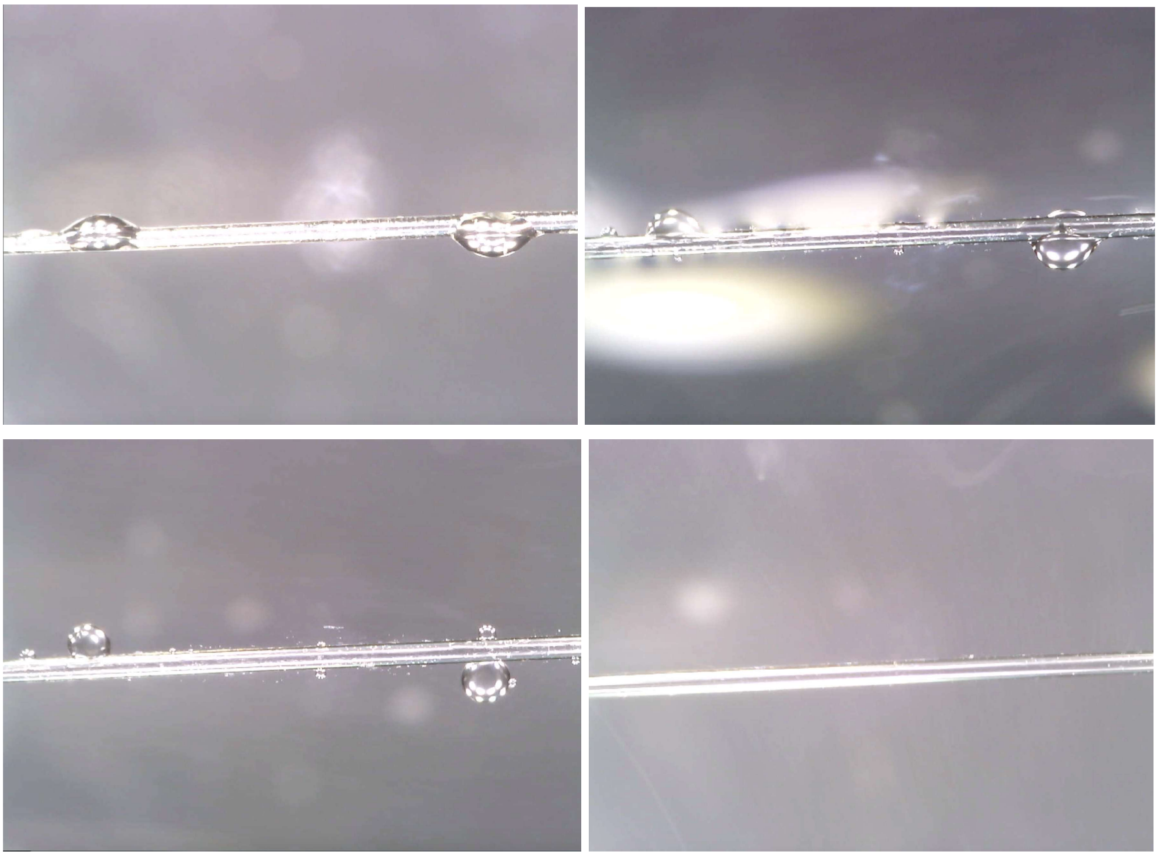

Figure 23. Microscopy images of a lyocell fiber in air, covered in olive oil. (upper left) The same fiber soaked in VIA Color Sensitive (upper right and lower left) again the same fiber in VIA Color Sensitive a couple of seconds later (lower right).

From these pictures it can be seen that the VIA Color Sensitive solution hits and encapsulates the olive oil droplet which in turn “roll up” and loosen from the lyocell fiber - demonstrating the so-called “roll up mechanism”.

4.4.3 Olive oil - SDS

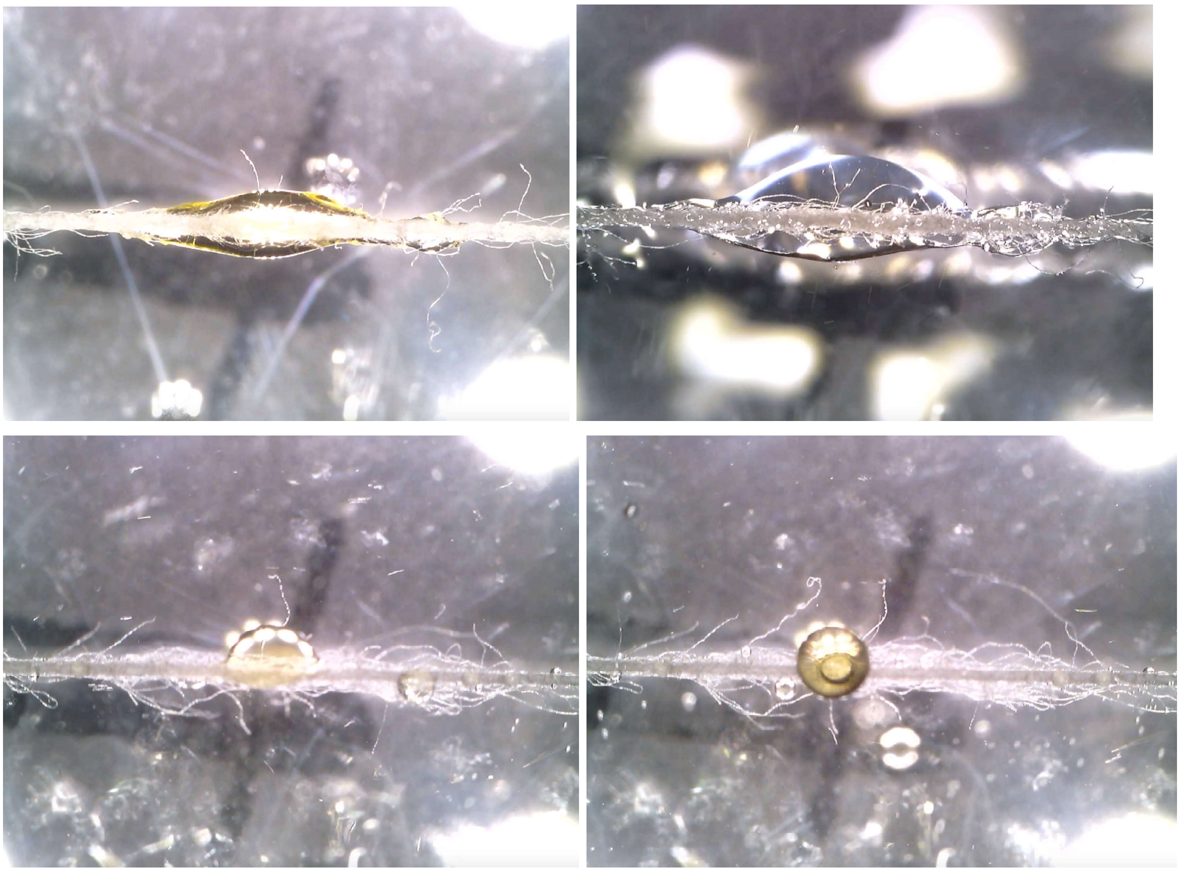

Figure 24. Microscopy images of a cotton fiber in air, covered in olive oil. (upper left) The same fiber soaked in SDS (upper right and lower left) again the same fiber in SDS a couple of seconds later (lower right).

From these images it can be seen that the SDS hits and encapsulates the olive oil droplet which in turn “roll up” and loosen from the lyocell fiber - demonstrating the so-called “roll up mechanism”.

4.4.4 Olive oil - tap water[1]

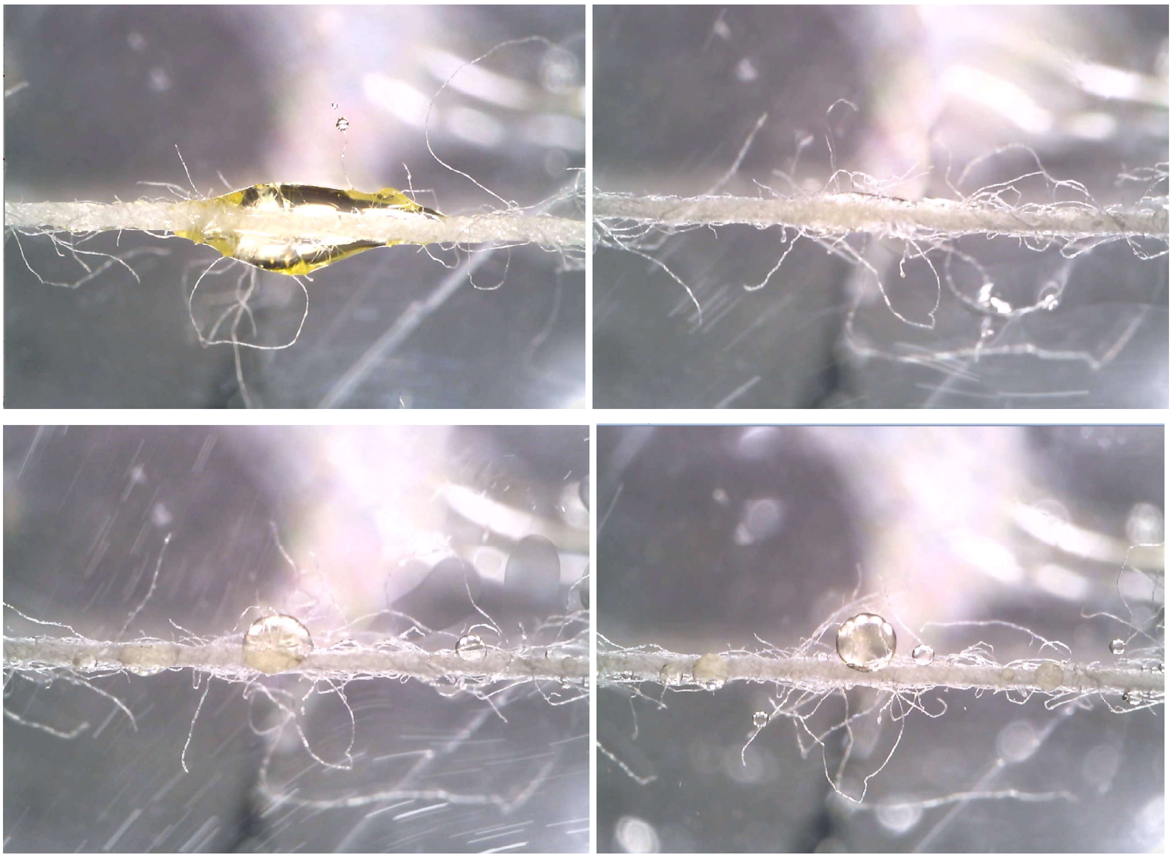

Figure 25. Microscopy images of a cotton fiber in air, covered in olive oil. (upper left) The same fiber soaked in tap water[1] (upper right and lower left) again the same fiber in tap water[1] a couple of seconds later (lower right).

From these pictures it can be seen that the tap water hits and washes over the olive oil droplet quickly. However, there is still olive oil left on the fiber which in time shape into oil bubbles sticking onto the cotton fiber.

5. Discussion

Cleaning is a complex process to fully understand and optimize, yet there are ways to compare available cleaning methods as long as they are evaluated under the same conditions. However, scientific standards evaluating the cleaning effect of a specific cleaning solution in terms of cleaning textiles and surfaces are scarce, or too vague. Instead, the QCM-D analysis was chosen as the surface cleaning test based on current research. Furthermore, the *EN 60456:2016* standard was chosen for laundry tests as this was recommended by people within the laundry industry. Cleaning tests of single fibres and emulsion tests were performed to visualize the cleaning mechanisms in real time as well as illustrate the colloidal chemistry mechanisms behind the cleaning processes.

From emulsion tests performed it is evident that the SDS solution disperse olive oil more efficiently than all other cleaning solutions tested. MQ water, DIRO® water and tap water[I] behave similarly in the separation from olive oil. However, looking closely it can be seen that MQ water (k=0,508) separates a bit slower than DIRO® (k=0,665) and tap water[I] (k=280) a bit faster than DIRO®. Hence, it seems like a higher level of water purity helps in a more efficient dispersion of olive oil. Furthermore, VIA Color Sensitive showed a dispersibility of the olive olive but not as high as the SAIW/Z-water. A reason for this could possibly be the alkaline condition in the SAIW soapifying the fatty acid within the olive oil creating its own surfactant from the olive oil.

The single fiber cleaning tests followed by optical microscopy showed that a solution of VIA Color Sensitive solved olive oil from a lyocell fiber more efficiently than DIRO® water did. The surfactants within VIA Color Sensitive encapsulated the olive oil droplets via micellation which made them soluble in the solution (Figure 23). The DIRO® water quickly washed away the olive oil droplets from the lyocell fiber. A possible explanation for this is the high surface tension of DIRO® water, contributing to a strong force on the oil droplets as the liquid front reaches the four phase line (air/water/oil/fiber). This phenomena forces the oil droplets away from the surface of the fiber. However, the oil re-attached to the fiber again after a couple of seconds in the shape of new small oil drops. This phenomena (Figure 22) clearly shows the action of the hydrophobic effect; water encapsulates the oil and avoids as much contact to the hydrophobic substance as possible.[19] Furthermore, the same phenomena can be seen for tap water (Figure 25). The water quickly washes over the olive oil droplet yet the olive oil sticks to the cotton fiber in the shape of drops. On the contrary, (Figure 24) shows how SDS efficiently washes over the olive oil droplets, encapsulates it and lets it rise to the surface of the liquid. Hence, there is a clear difference between surfactant based cleaning solutions and non-surfactant based cleaning solutions in terms of cleaning mechanisms.

Laundry tests showed a similar pattern for both 40℃ and 60℃ washes. The reference detergent was pre-eminent in cleaning performance for all soils while VIA Color Sensitive showed the overall second best effect. VIA Color Sensitive performed better than all water types for carbon, cocoa and most of all blood. However, VIA Color Sensitive showed the lowest performance on wine and a relatively low performance on sebum. To fully evaluate why the cleaning agents performed differently for different soils it is important to know exactly what is in the soils (see Appendix 9.5). VIA Color Sensitive is, as the name suggests, a detergent aimed for colored textiles. Hence, there are no bleaching agents within this detergent. This could be the reason for the low performance on the red wine. The sebum result is more strange as a detergent based on surfactants should be able to solve fat to some extent. However, not knowing the full program composition of the laundry machines used for this detergent leaves many unknown factors worth investigating to fully understand these results.

Overall, Z-water seems to demonstrate the overall lowest cleaning performance of all cleaning solutions and all temperatures tested. Even though there seems to be no significant difference in the overall performance compared to tap water there was a significantly lower result compared to DIRO® water. However, Z-water showed the best cleaning result on the blood stain even though this result was clearly the lowest of all cleaning solutions for that specific stain. This result is probably due to the presence of hemoglobin in the blood. An alkaline solution such as SAIW will change the structure of hemoglobin from oxygenated to deoxygenated, which in turn affects its solubility and its color. Deoxygenated hemoglobin is less soluble in water and also shows a darker red color. This darker red color can be observed for the blood stain washed in SAIW. Z-water had the lowest performance on the cocoa stain. With that said, the program used for Z-water was 10 min shorter than those of DIRO®/tap water[II]. It should also be noted that less washing cycles were done with Z-water. [25]

Tap water[II] and DIRO® performed very similarly in the laundry cleaning performance. Overall, it can be stated that there is no significant difference in laundry cleaning efficiency of DIRO® and tap water from the laundry tests performed in this project. However, looking at each individual soil it can be said that DIRO® had a slightly higher performance for sebum, carbon and wine in 60℃ and for carbon and wine in 40℃. Although this difference in performance is minimal, it is worth mentioning. For the cleaning performance on each individual soil see Appendix 9.3.

The results from the surface cleaning analysis (QCM-D) differed completely from the results of A. Tsompou and V. Kocherbitov at Malmö University.[20] A. Tsompou and V. Kocherbitov suggested that the QCM-D analysis shows a measurement error of ± 20 Hz in resonance frequency. Results in this study showed a higher error. Measurements of a bare crystal in air and MQ water showed an average error of ± 24,6 Hz, (Figure 12). Furthermore, sharp QCM-D measurements with a Vaseline coating also showed different results than those of A. Tsompou and V. Kocherbitov.[20] In this study, tap water[I] removed 95,5% of the Vaseline solution, followed by SAIW (87,5%), MQ water (86,5%), SDS (80,5%) and DIRO® (77,3%). According to A. Tsompou and V. Kocherbitov, both DIRO® and MQ removed > 90% Vaseline whilst tap water removed 75% and SDS removed 100%.[20]

Naturally, the concentration and thickness of Vaseline compared to the study performed at Malmö University differed by a factor of 5, which is probably the reason for these result differences. In addition, QCM-D is a very sensitive analysis technique where thick crystal layers may disturb its performance. However, the layer thickness used by A. Tsompou and V. Kocherbitov needed no further QCM-D analysis since this layer completely disappeared just by dipping a silica wafer (with that specific coating) in water. Hence, a higher concentration and thickness was chosen in this project.

Another important factor to mention here is how the "washed" crystals were treated between measurements. A. Tsompou and V. Kocherbitov rinsed the already washed crystal with Milli-Q water followed by drying. In this project there was no additional rinsing of the crystal, only blow drying with N_2 gas. Worth mentioning is also that some liquid was still present on the crystals when disabled from the chamber after "wash". This liquid was difficult to dry since the liquid front would not leave the quartz surface (Appendix 9.1; Figure 26). Nevertheless, the QCM-D results in this study indicates that a large amount of Vaseline disappears using all cleaning solutions.[20] A possible explanation for this is the same scenario as in the cleaning tests of the individual fiber. The high surface tension of tap-, DIRO® - and MQ water seem to contribute to a strong force on the hydrophobic Vaseline as the cleaning liquid front reaches the four phase line (air/water/Vaseline/crystal). This phenomena forces the Vaseline away from the surface of the silica crystal.

What is further interesting to note in this study is that DIRO® water does not fulfill many of the facts found about this cleaning product. According to the manufacturers[26], washing with DIRO® is just as efficient as traditional detergents but more energy efficient. However, the DIRO® water did not show the same cleaning performance as VIA Color Sensitive or the reference detergent. In addition, the DIRO® system consumes more energy than a regular Electrolux W465H laundry machine. Thus, the statements made by the manufacturers of DIRO® water seem incorrect.

DIRO® water is also said to have a long storage time[26]. While this statement is rather vague it is not valid regarding DIRO® water stored in plastic containers (DIRO® spray bottle), according to measurements made in this study. As demonstrated here, DIRO® water loses its ultra pure characteristics when stored in a plastic bottle. The conductivity of this DIRO® water increased from 0,686 µS/cm to 532 µS/cm in less than a month. This value is higher than the conductivity for regular tap water used in this study (280 µS/cm). DIRO® water is sold to be stored in plastic containers. Thus, this type of distribution and storage is worth questioning. Furthermore, A. Tsompou and V. Kocherbitov stated that the DIRO® water used in their study was stored in a plastic bottle for one month before measurements took place. Their documented conductivity value of DIRO® was 1,51µS/cm.[20][26] Hence, their storage time of DIRO® seems questionable.

While the cleaning ability of UPW is widely discussed in scientific research, especially within the semiconductor industry, there is no scientific proof of its ability to efficiently clean textiles in a laundry machine. Researchers at Linköping University demonstrated a UPW cleaning agent called QW with a conductivity of 0,03-0,04 µS/cm. However, it is stated that the QW is used to clean printed circuit boards, front of buildings and hydroelectric dams. In addition, it is stated that the cleaning ability of QW quickly decreases with increased conductivity. In fact, the cleaning ability vanishes completely once a conductivity value of 0,05 µS/cm is reached.[7] If that is to be true, none of the UPW types used in this study would be suitable cleaning solutions. Likewise, researchers at ANU discuss the possibility of UPW as a future cleaning product, however the UPW demonstrated in their study is highly degassed, with a very low conductivity.[17]

As mentioned in the introduction, a value of 100% water purity is theoretically achievable but not possible to maintain due to the direct contamination by air or other appliances in contact with the water. A purified water will be highly reactive and solve almost everything that comes its way. Thus, pipes and other appliances of delivery require proper design, where choice of material, flow and pressure is crucial. Moreover, resistivity will decrease when water is stirred or sprayed as these actions will intensify contamination from the atmosphere.[8],[13] Hence, selling UPW to be stored and used in plastic spray bottles is not very efficient to maintain its quality. Furthermore, Merck KGaA, a world wide producer of MQ water even suggests to not store UPW due to contamination and the tendency of stagnant water to grow bacteria or algae. Even the tubing, installed for distribution of the water could be a source of bacterial/algae development if droplets are left in the system. Tubing of plastics even constitutes a risk of plasticizer leaching.[27]

Although the findings by researchers at Linköping and ANU are promising, it is highly difficult to maintain and control that kind of water purity. Moreover, it has been stated that UPW targets polar and ionic substances, never non-polar, as this type of dissolution is a direct effect of changes in entropy even though the enthalpy changes might be favourable.[9] Hence, UPW might be effective during certain cleaning processes, but not in all cases.

With that said, traditional detergents are not problem free due to negative impacts on the environment. Thus, it is important to further investigate possible alternatives to traditional detergents. However, from a health point of view, effective detergents are necessary. Thus, implementing a UPW cleaning technology that is not yet fully understood or scientifically proven is alarming and nowhere near revolutionary.

6. Conclusions

Several tests have been conducted in this study to evaluate the cleaning effect of UPW compared to SAIW, traditional detergents and most importantly tap water. UPW is widely used for cleaning within the semiconductor industry where it effectively desorb particles from micro devices. Now, it has been proposed that UPW is as efficient as traditional detergents in terms of cleaning both textiles and a wide range of surfaces. While this suggestion sounds good in theory, it does not seem to work in practice.

UPW tested in this study showed a significantly lower performance in cleaning textiles compared to traditional detergents based on surfactants. Overall, there was no significant difference between the soil removal performance of tap water and UPW in conducted laundry tests. Surface cleaning tests showed that UPW removed 77,3% Vaseline from a silica surface while tap water removed 95,5%. However, these QCM-D results should be interpreted with caution as the coating thickness of Vaseline used within this study seems to have affected the analysis in an unknown way. Finally, cleaning tests on single fibers demonstrated the inability of UPW to solve hydrophobic drops of olive oil while emulsion tests showed a hint of dispersion for UPW in comparison to tap water but still a clear separation to olive oil.

In conclusion, UPW of high quality is “highly reactive” and may solve both polar and ionic substances but not nonpolar. There is research pointing towards a “cleaning effect” of UPW with very low conductivity, yet these claims still require more research. Thus, UPW possibly aimed for cleaning should be highly degassed and/or carefully stored/distributed to maintain a high purity with very low conductivity. However, UPW such as DIRO®- and MQ water used in this study are not even near these requirements. Thus, no major cleaning effect was observed.

7. Further research

Further research should be conducted to fully understand the possible cleaning mechanism of certain types of UPW. A variation of cleaning tests should be performed using a larger sample size to ensure even more accurate results. Finally, the DIRO® technology should be investigated to determine the actual water quality at different applications.

8. References

1. Miele Professionals. *Sinner's Circle: For a hygienic wash cycle.* **2019.**

2. Levey, M. The early history of detergent substances: A chapter in Babylonian chemistry. *Journal of Chemical Education.* **1954**, *31*, (10).

3. American Cleaning Institute. SOAPS & DETERGENTS HISTORY. https://www.cleaninginstitute.org/understanding-products/why-clean/soaps-detergents-history

4. Beiras, R. Marine Pollution: Chapter 3 - Nonpersistent Inorganic Pollution. **2018**, p 31-39.

5. Cassidy, C. Who Discovered Soap? What to Know About the Origins of the Life-Saving Substance. *TIME Magazine*. https://time.com/5831828/soap-origins/

6. Ivanković, T and Hrenović, J. Surfactants in the Environment. *Archives of Industrial Hygiene and Toxicology.* **2010**, *61*, (1), p 95-110.

7. Lindahl,M; Svensson, N; Svensson, B et al. Industrial cleaning with Qlean Water – a case study of printed circuit boards. *Journal of Cleaner Production.* **2013**, *47,* p 19-25.

8. Melnik, L.A and Krysenko, D.A. Ultrapure Water: Properties, Production, and Use. *Journal of Water Chemistry and Technology.* **2019**, *41*, (3), p 143–150.

9. Ohmi, T. Ultra-Clean Technology Handbook. **1993.**

10. Light, T; Licht, S; Bevilacqua, A et al. The Fundamental Conductivity and Resistivity of Water *Electrochemical and Solid-State Letters*. **2005**, *8,* (1).

11. Gupta, P; Rahm, C; Jiang, D et al. Parts per trillion detection of heavy metals in as-is tap water using carbon nanotube microelectrodes. *Analytica Chimica Acta.* **2021**, *1155*.

12. Pashley, R; Rzechowicz, M; Pashley, L et al. De-Gassed Water Is a Better Cleaning Agent. *The Journal of Physical Chemistry B.* **2005**, *109,* (3), p 1231-1238.

13. Hutcheson, J. Ultrapure water: systems for microelectronics. *Filtration & Separation.* **2006**, *43,* (5), p 22-25.

14. Lee, H; Jin, Y and Hong, S. Recent transitions in ultrapure water (UPW) technology: Rising role of reverse osmosis (RO). *Desalination*. **2016**, *399*, p 185-197.

15. Regnault, C; Kano, I; Darbouret, D et al. Ultrapure water for liquid chromatography–mass spectrometry studies. *Journal of Chromatography A*. **2004**, *1030,* (1-2), p 289-295.

16. ORGANO. About pure water and ultrapure water. **2018.** https://www.organo.co.jp/english/purewater/

17. Francis, M and Pashley, R. The effect of de-gassing on the dispersion of fine oil droplets in water. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.* **2006**, *287,* (1-3), p 36-43.

18. Francis, M; Gulati, N and Pashley, R. The dispersion of natural oils in de-gassed water. *Journal of Colloid and Interface Science.* **2006**, *299,* (2), p 673-677.

19. Eastoe, J and Ellis, C. De-gassed water and surfactant-free emulsions: History, controversy, and possible applications. *Advances in Colloid and Interface Science.* **2007**, *134-135,* p 89-95

20. Tsompou, A and Kocherbitov, V. The effects of water purity on removal of hydrophobic substances from solid surfaces without surfactants. *Journal of Colloid and Interface Science*. **2022**, *608,* p 1929-1941.

21. Suzuki, Y; Hishiki, T; Emi, A et al. Strong alkaline electrolyzed water efficiently inactivates SARS-CoV-2, other viruses, and Gram-negative bacteria. *Biochemical and Biophysical Research Communications.* **2021**, *575,* p 36-41.

22. Z-water.se

23. Biolin Scientific. OCM-D: An Overview of Technology and Measurements. **2020.**
https://www.biolinscientific.com/measurements/qcm-d#what-is-qcm-d

24. EN 60456:2016; Clothes washing machines for household use – Methods for measuring the performance. **2016.**

25. Huang, Y et al. Pathway and Mechanism of pH Dependent Human Hemoglobin Tetramer-Dimer-Monomer Dissociations. *PLOS ONE*. **2013**, *8,* (11).

26. SWATAB: DIRO.
https://swatab.com/diro/ 2023-05-01

27. Riche, E and Mabic, S. The Do's and Don'ts of Working with Purified Water. *Merck KGaA*. **2018.**
https://theanalyticalscientist.com/fileadmin/tas/issues/App_Notes/08018-Merck-ROW-app-note-supplied.pdf

28. Callaghan, M.A et al. Plasticizers and Cardiovascular Health: Role of Adipose Tissue Dysfunction. *Frontiers in Pharmacology.* **2021**, *11.*

9. Appendix

9.1 Additional QCM-D information

Figure 26. QCM-D crystal after "wash" showing a persistent "sticking" liquid drop present on the analyzed surface.

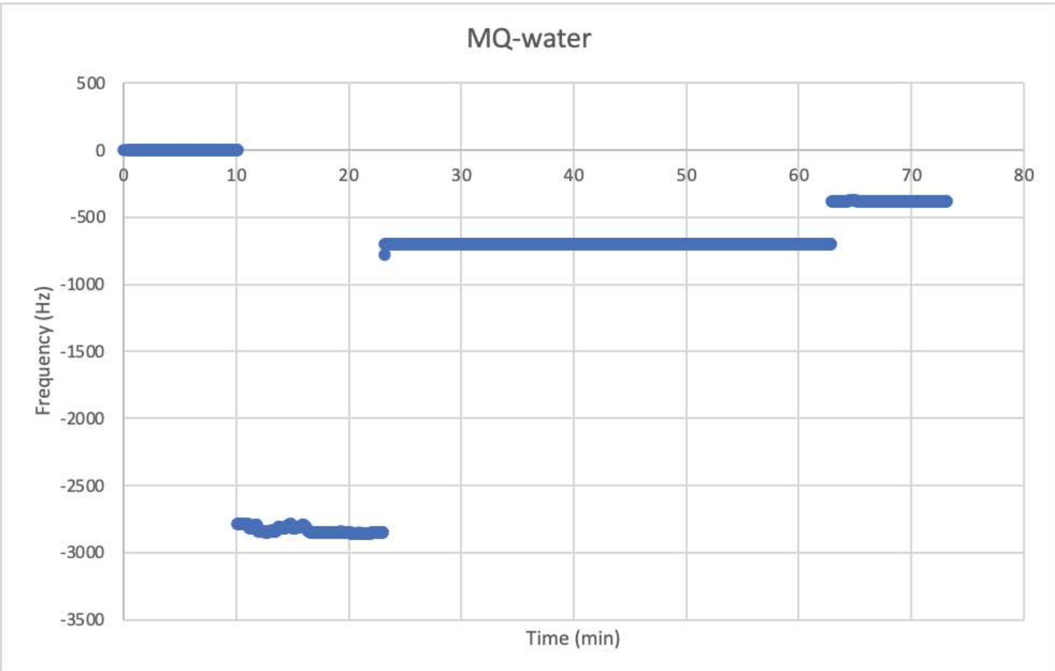

Figure 27. QCM data (3rd overtone) for MQ water, showing Δf/n as a function of time as the crystal went from bare to coated, introduced to liquid and finally dried.

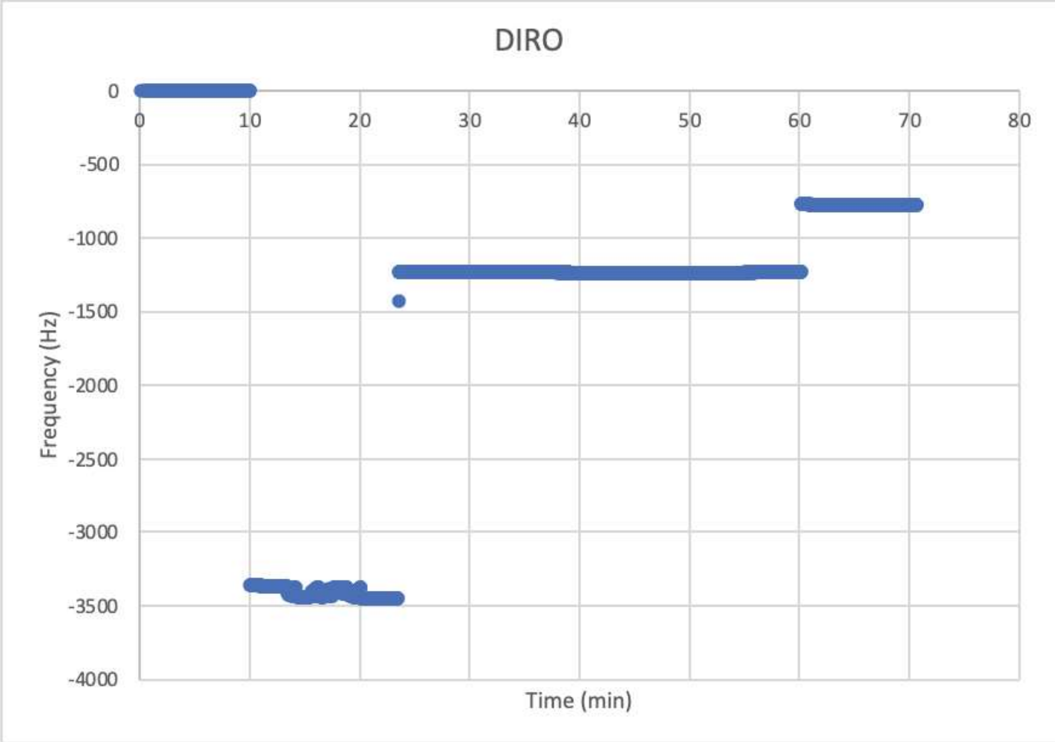

Figure 28. QCM data (3rd overtone) for DIRO® water, showing Δf/n as a function of time as the crystal went from bare to coated, introduced to liquid and finally dried.

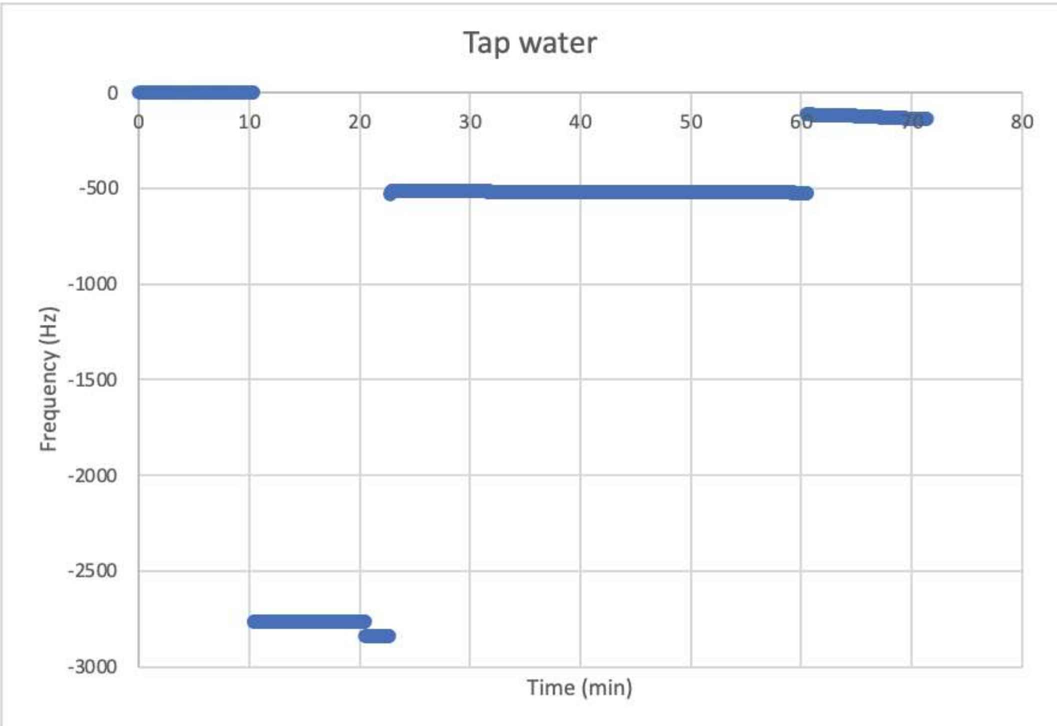

Figure 29. QCM data (3rd overtone) for tap water[1], showing Δf/n as a function of time as the crystal went from bare to coated, introduced to liquid and finally dried.

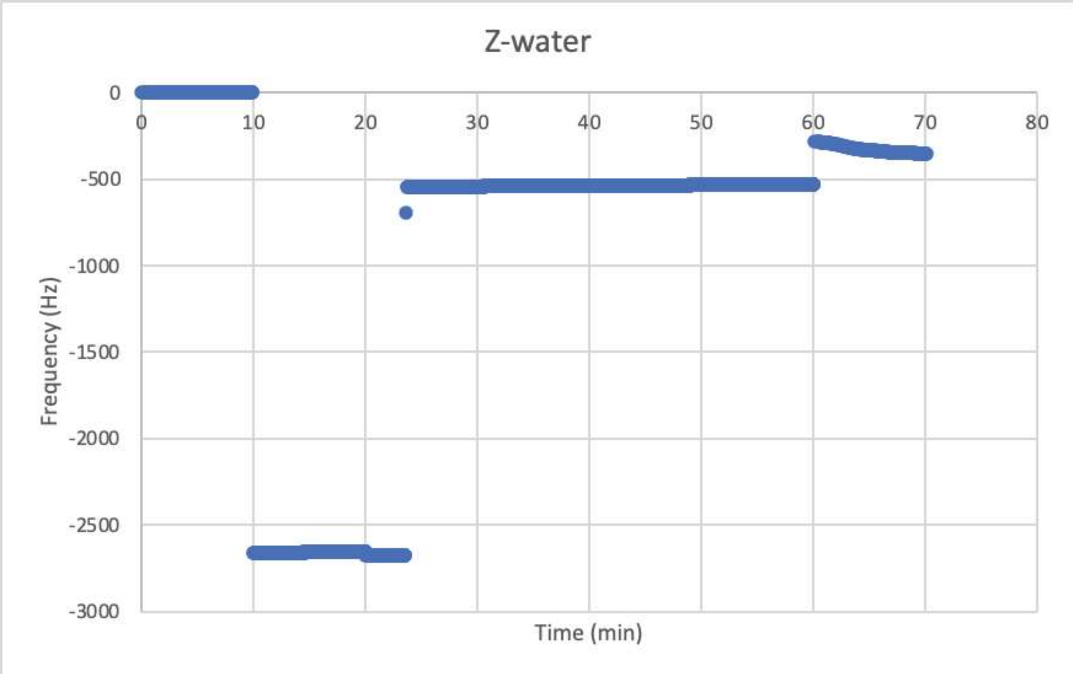

Figure 30. QCM data (3rd overtone) for Z-water, showing Δf/n as a function of time as the crystal went from bare to coated, introduced to liquid and finally dried.

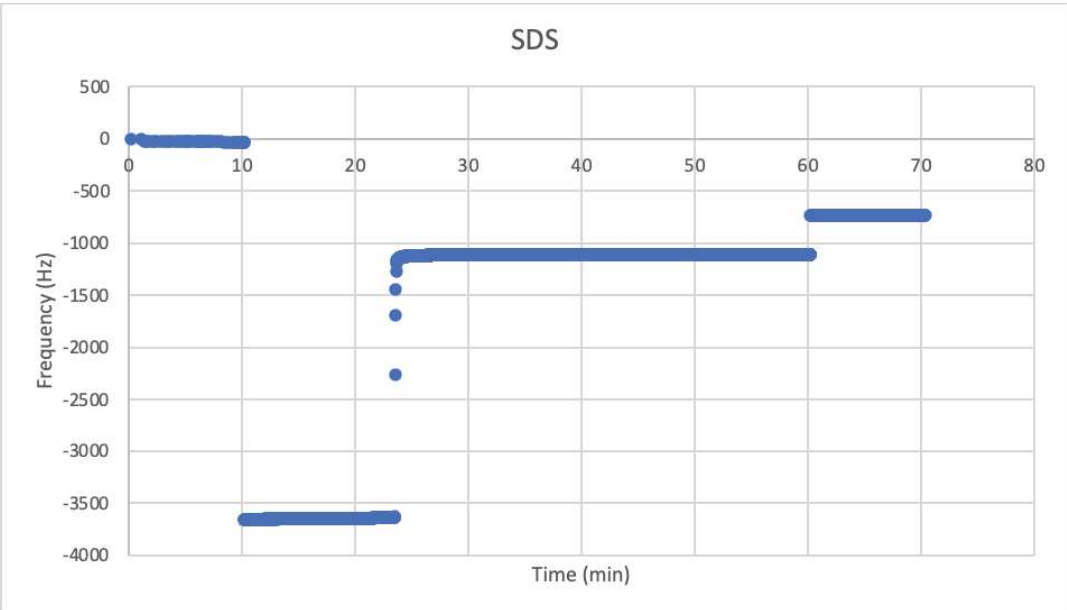

Figure 31. QCM data (3rd overtone) for SDS, showing Δf/n as a function of time as the crystal went from bare to coated, introduced to liquid and finally dried.

9.2 Laundry test analysis - statistical calculations

To summarize the laundry test, each washing liquid was tested in three different washes. In each washing machine 4 different stained stripes were added per wash. Each of the stain spots on each individual stain square was measured 4 times.
For each measured point of reflectance (out of 4 points per soil square) was compared to the reflectance value before wash for that individual stain using equation 2. This gives 4 individual q-values for each soil square analyzed. The average q-values for each soil square and temperature was calculated together with the standard deviation for the respectively different stains that was calculated using error of propagation, (equation 3).
Furthermore, pooled standard error was used to determine the final standard deviation for each stain in the laundry test (4 x 3), (equation 4).

$$\frac{C_{test}}{C_{ref}} = q \tag{2}$$

$$error\ of\ propagation = \sqrt{(-\left(\frac{C_{test}}{{C_{ref}}^2}\right) \cdot st\ dev_{ref})^2 + (\frac{1}{C_{ref}} \cdot st\ dev_{test})^2} \tag{3}$$

$$pooled\ standard\ error = \sqrt{\left(\frac{\left(st\ {dev_1}^2 + st\ {dev_2}^2 + ..\right)}{n}\right)} \tag{4}$$

The standard deviation for the overall sum average was calculated with the same type of pooled standard error (4).

9.3 Additional data for washing at 40℃

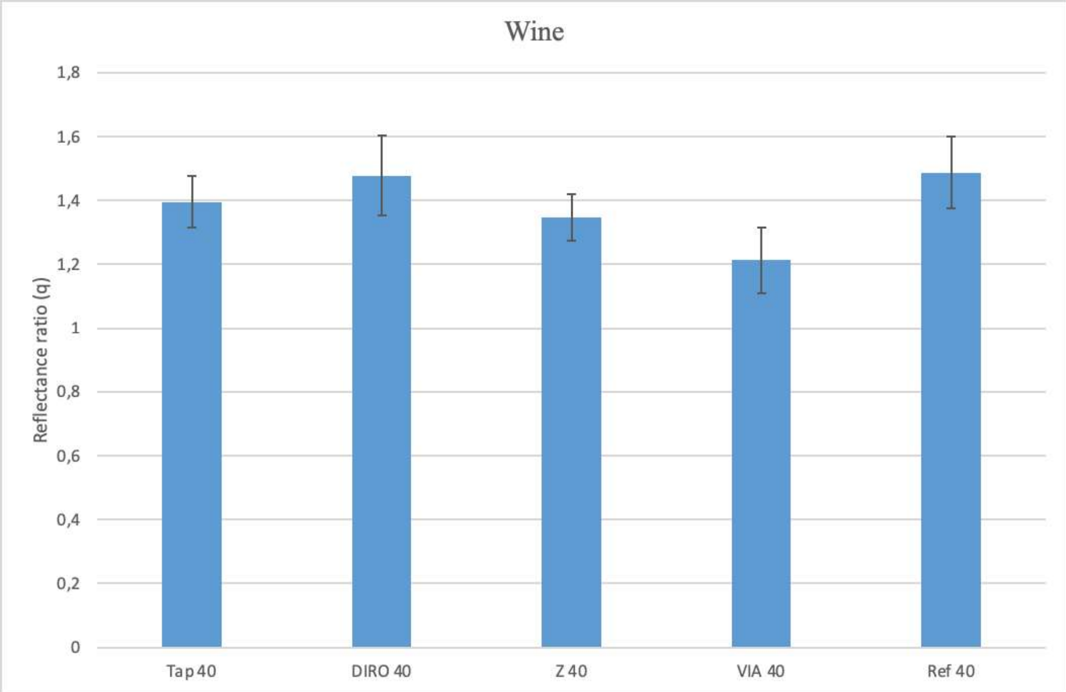

Figure 32. Reflectance ratio for WINE for all cleaning agents at 40℃.

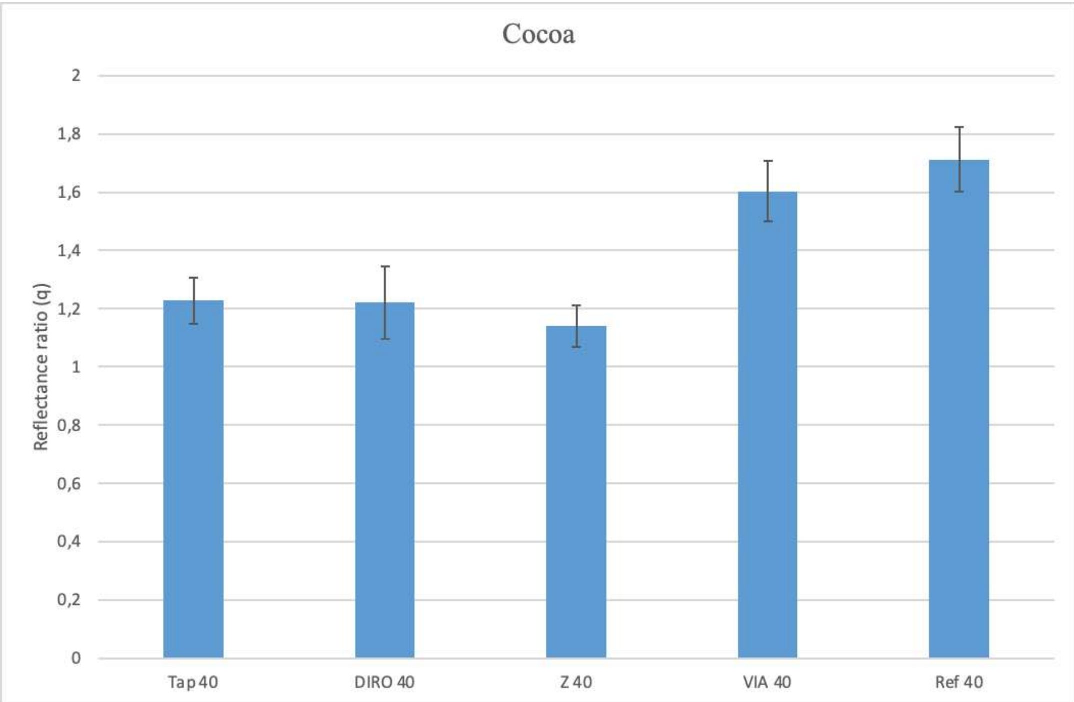

Figure 33. Reflectance ratio forCOCOA for all cleaning agents at 40 ℃.

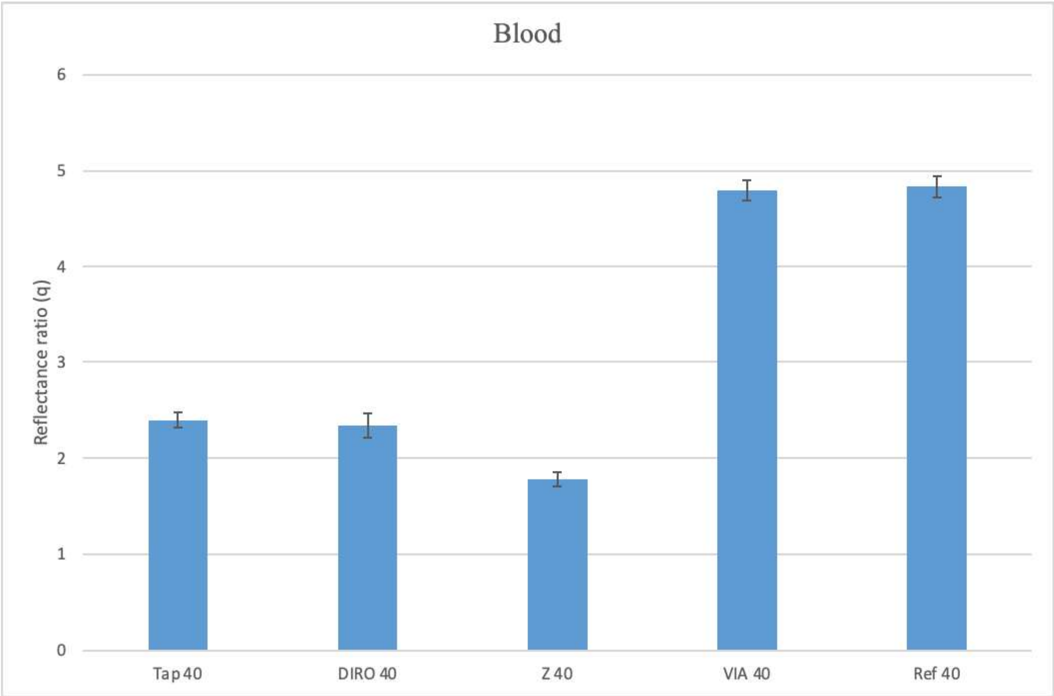

Figure 34. Reflectance ratiofor BLOOD for all cleaning agents at 40℃.

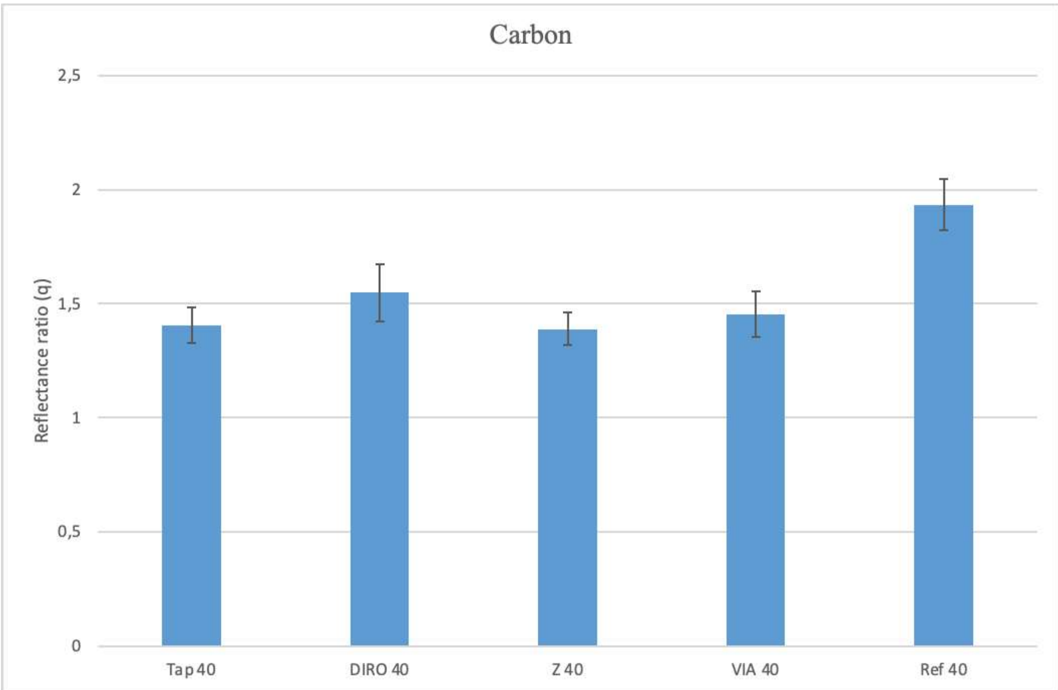

Figure 35. Reflectance ratio for CARBON for all cleaning agents at 40 ℃.

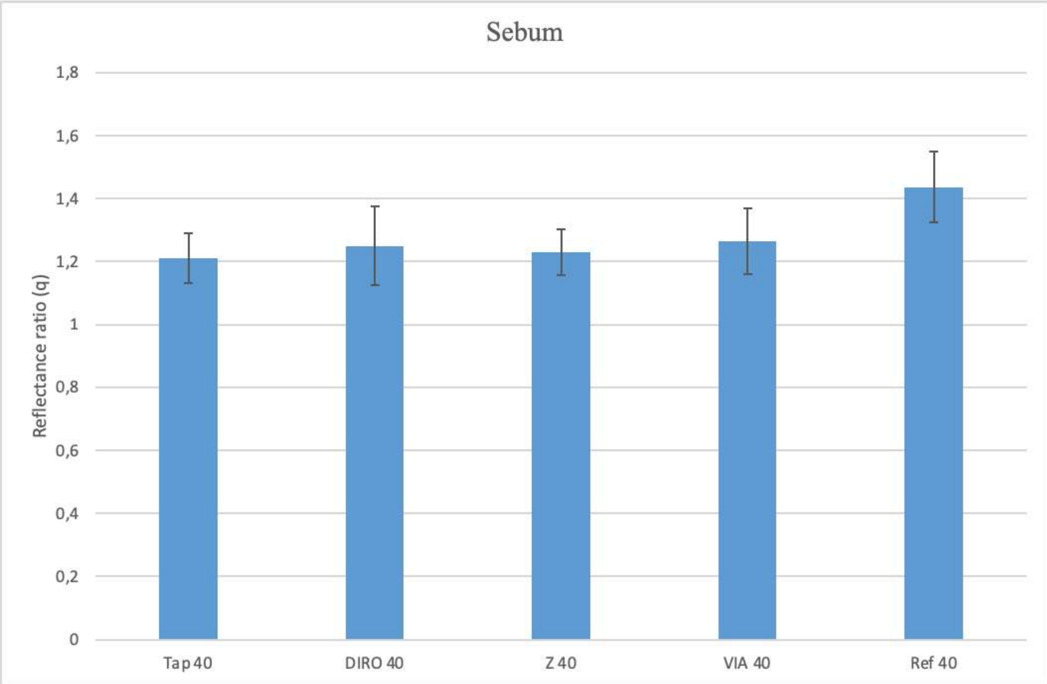

Figure 36. Reflectance ratio for SEBUM for all cleaning agents at 40 ℃.

9.4 Additional data for washings at 60℃

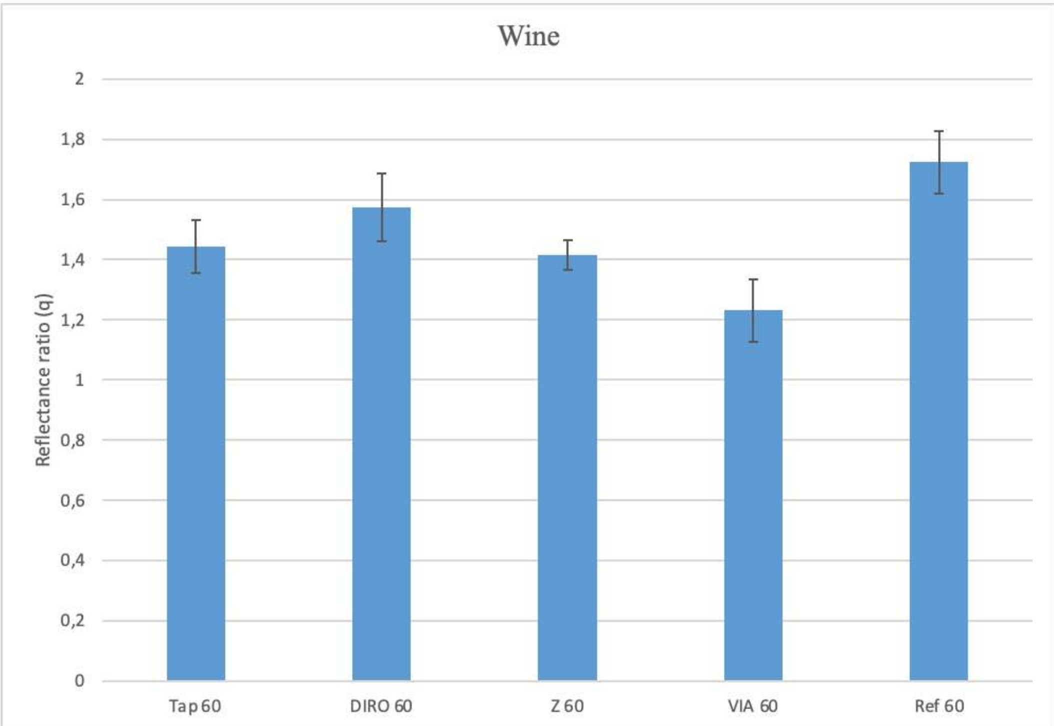

Figure 37. Reflectance data WINE for all cleaning agents at 60 degrees.

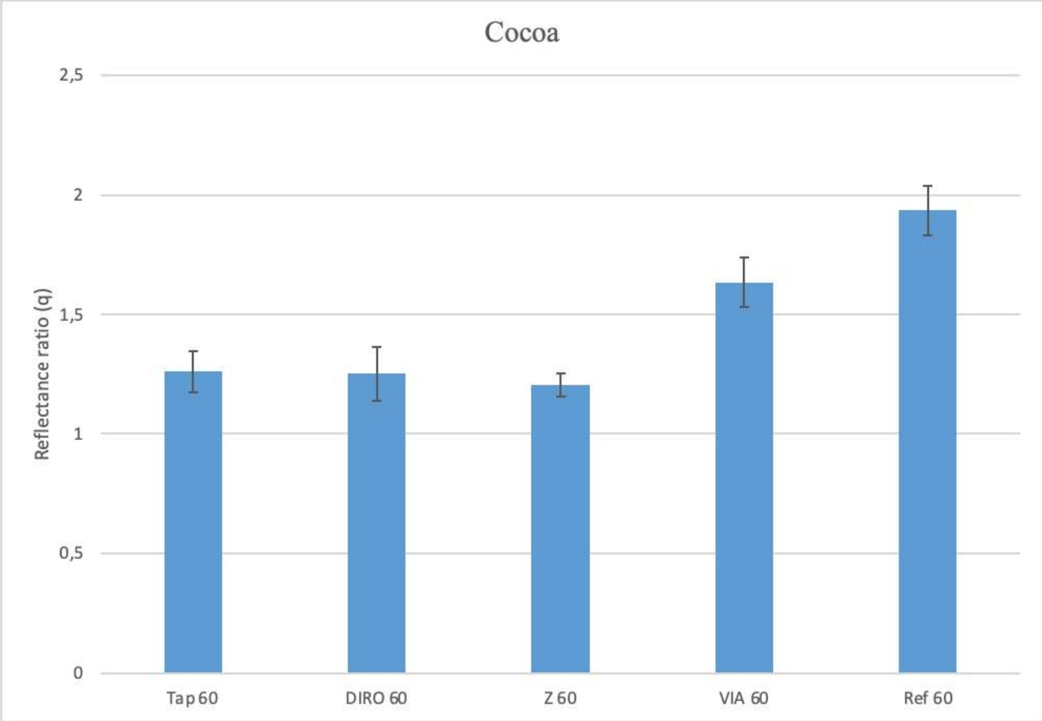

Figure 38. Reflectance data COCOA for all cleaning agents at 60 degrees.

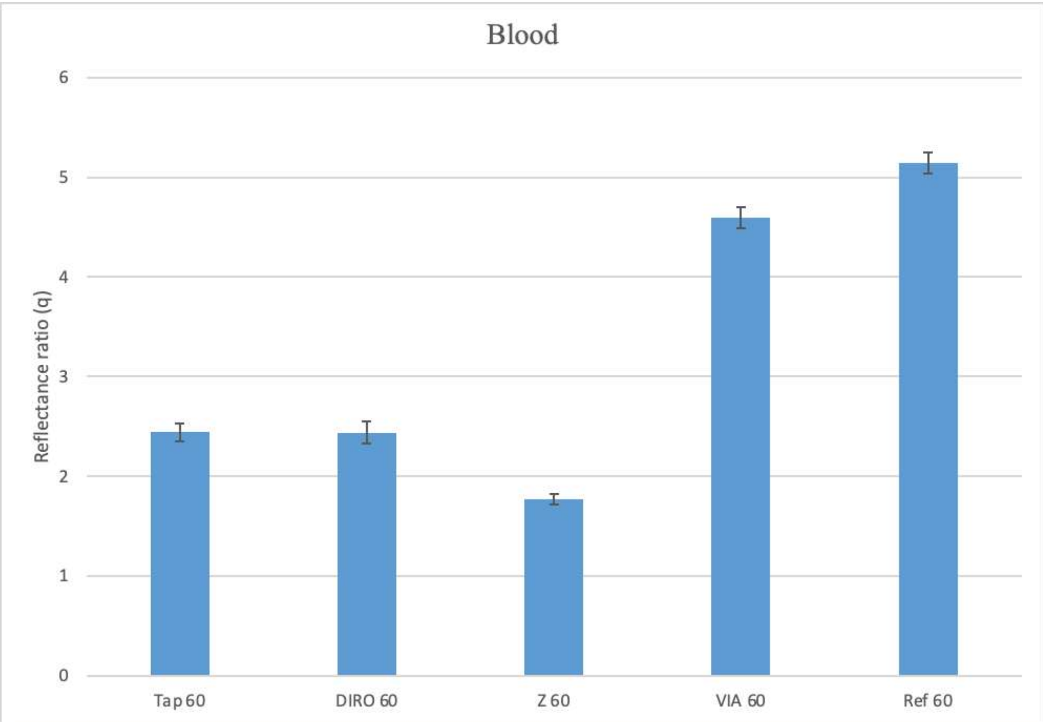

Figure 39. Reflectance data BLOOD for all cleaning agents at 60 degrees.

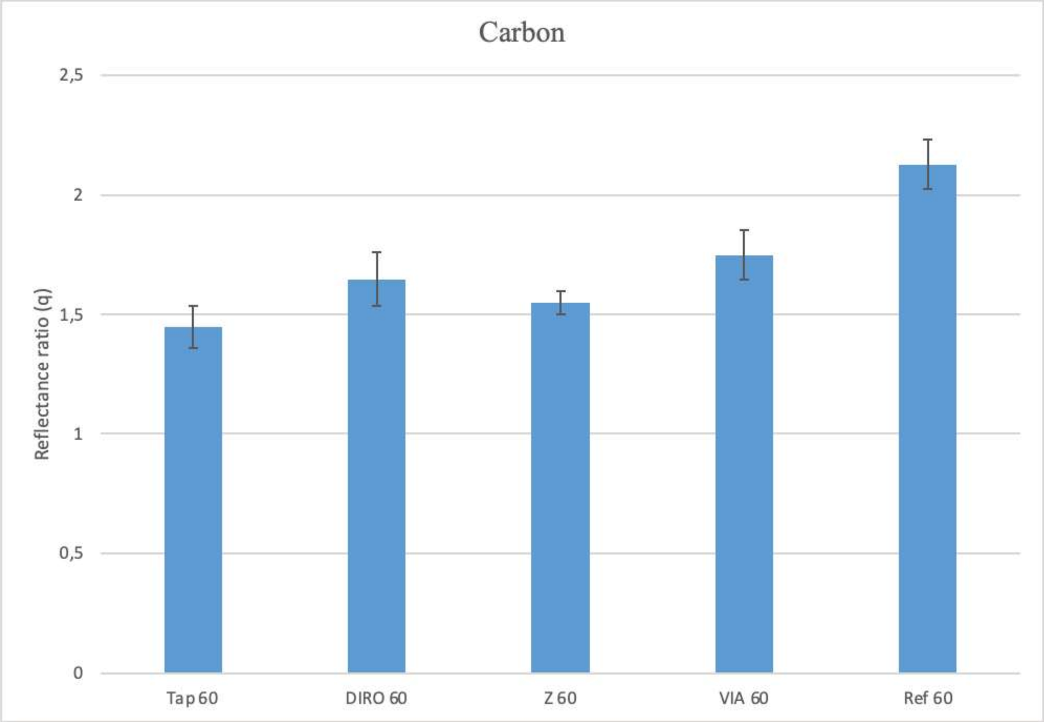

Figure 40. Reflectance data CARBON for all cleaning agents at 60 degrees.

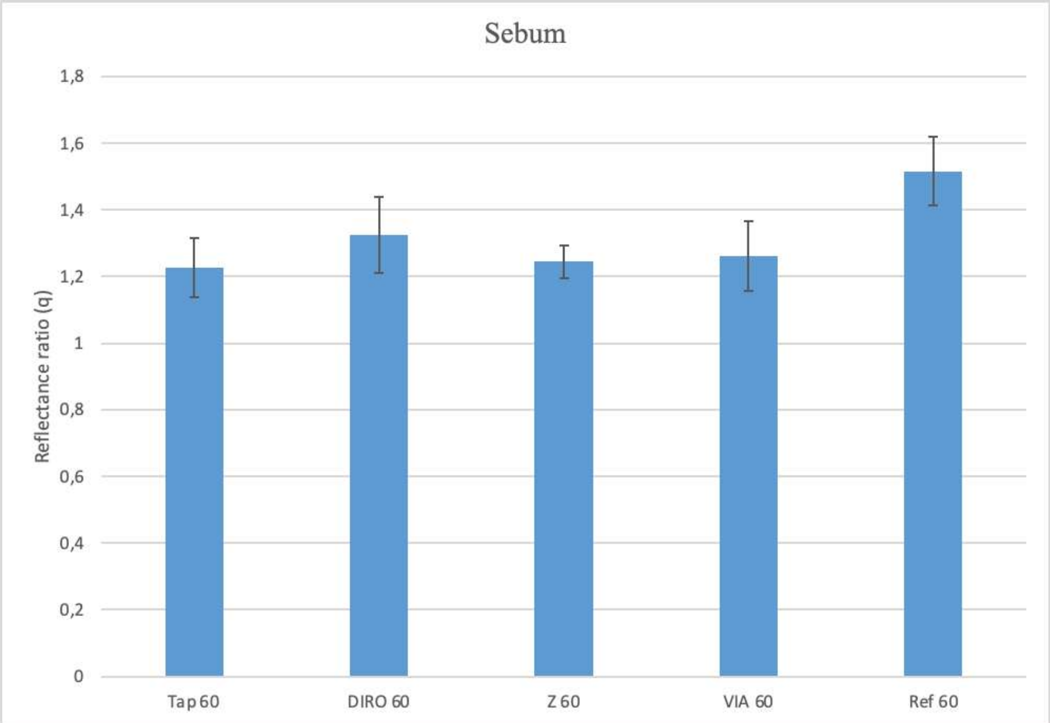

Figure 41. Reflectance data SEBUM for all cleaning agents at 60 degrees.

9.5 Stain strip soil composition

Table 14. Soil composition according to EN 60456:2016.

Sebum	
Synthetic sebum composition	Cows fat : 32,8 % Wool fat : 18,3 % Free fatty acid : 18,0 % Cholesterol : 3,7 % Squalen : 8,9 % Coconut oil : 3,6 % Hard paraffin : 3,1 %
Pigment	Carbon black Kaolin Iron oxide (yellow and black)
Carbon	
Oil	Paraffin oil
Pigment	Carbon black (96% carbon)
Blood	
Composition	Fresh pig's blood and 10 g/l ammonium citrate (stabilizer)
Cocoa	
Composition	Unsweetened cocoa (20/22 % fat, not alkalised) with sugar, full-cream cow's milk and water.
Wine	
Composition	Red wine; "Alicante" (treated with hot air)

9.6 Adjusted washing program for DIRO® and tap water[II]

Table 15. Washing program programmed for DIRO®.

Program	*"Normal 40"*	*"Normal 60"*	Note
Prewash (optional)	6 min	6 min	
Wash 1	5 min	5 min	
Centrifuge	0,5 min	0,5 min	600 rpm
Wash 2	8 min	8 min	
Rinse			Change of water
Wash 3	8 min	8 min	Heating
Rinse			Change of water
Wash 4	8 min	8 min	
Ending Centrifuge			

9.7 Washing programs for PODAB ProLine HX 65 (Z-water)

Table 16. Washing program programmed for SAIW / "Z-water".

Program	*"Normal 40"*	*"Normal 60"*	Centrifuge	Note
Prewash	5,5 min	5,5 min	400/1 minute	30 °C
Wash 1	7 min	23,5	400/1 minute	40 °C
Rinse	6,5 min	6,5 min	400/1 minute	Change of water
Rinse 2	6,5 min	6,5 min	1165/9 minute	Heating and change of water
Ending tumbling	0,5 min	0,5 min		

9.8 Plastic DIRO® bottle

Figure 42. DIRO water stored in plastic bottle (left) and glass bottle (right).

.