

## **ABSTRACT**

GIRASE, ARJUNSING. Evaluation and Improvements of Cleaning Methodologies practiced in the Firefighting Community (Under the direction of Dr. Bryan Ormond).

Firefighters are exposed to several potentially carcinogenic fireground contaminants at every fire scene. The continuous exposure includes a concoction of the chemicals that include volatiles and semi-volatiles. The terms “firefighter” and “cancer” are used frequently together due to the research findings that link occupational exposure to the different types of cancer. The current NFPA 1851 washing procedures are less effective in cleaning these procedures due to the limited intensity of the washing procedures that are used. The residual contamination can pose a severe threat to the health of the firefighters.

The limited information that was available through research in this domain included the types of contaminants and the inefficacy of the washing procedures. However, different research findings demonstrated different decontamination efficacy. A thorough evaluation of the analysis of the actual samples from the turnout suits was needed. The major research gap was the absence of a standard test procedure to evaluate the parameters that have a significant impact on the decontamination of the turnout suits. The fundamental area that was addressed by this research was the evaluation of the washing procedures by studying the different washing parameters. A bench-scale washing procedure was developed that included controlled contamination, washing and extraction of the samples using a pressurized solvent extractor. The validation of all the steps showed that the method was consistent and efficient. The comparative studies of bench-scale with full-scale experiments were performed to understand the deviation of bench-scale washing procedures from the full-scale washing experiments. The results demonstrated low deviation

from the full-scale. Following the results, bench-scale testing of various surfactants was performed to improve the decontamination efficiency of the turnout suits.

The use of liquid CO<sub>2</sub> in laundering has garnered attention in recent years due to its higher cleaning efficacy and eco-friendliness. A comparative study of the conventional wash and liquid CO<sub>2</sub> method was performed on the turnout jackets. The conventional method used was the method set according to the NFPA 1851 standard and for liquid CO<sub>2</sub> a commercially available method was used. The CO<sub>2</sub> washing showed a considerable improvement in washing efficiency compared to the conventional wash.

Comparative studies on real-world samples were done to further investigate the decontamination efficiency of different washing techniques. The fire department of New York and Broward County fire department gears were used in the studies. All the samples were distributed into different categories and were subjected to different cleaning techniques. The comparison of pre and post-wash analysis indicated that liquid CO<sub>2</sub> cleaning performed better as compared to the other methods.

The final aim of the research was to investigate the impacts of modified washing techniques have on the durability of the turnout suits. The samples were prepared using outer shell material to emulate turnout suits. The samples were washed with 15 and 30 washes using different washing techniques. For a baseline comparison, conventional washing was included as one method. The results were compared with the unwashed samples to further investigate the results. It was found that higher washing temperatures and longer washing durations can have a harsh impact on the outer shell material, liquid CO<sub>2</sub> affected the reflective trims and color labels to some extent.

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Evaluation and Improvements of Cleaning Methodologies practiced in the  
Firefighting Community

By  
Arjunsing Girase

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APPROVED BY:

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Dr. Bryan Ormond  
Committee Chair

---

Dr. Donald B. Thompson

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Dr. Blanton Godfrey

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Dr. Roger L. Barker

## **DEDICATION**

This dissertation is dedicated to the first responders all over the world who protect society by their constant vigilance.

This dissertation is also dedicated to:

- To my parents, Archana and Gajendrasing, for everything that they have done for me. Without them, all this would not have been possible.
- To my brother Karansing, who has been a huge support to me throughout my life.
- To all my teachers till now who have guided me on this golden path of education
- To Monica, for constantly pushing me out of my comfort zone and listening patiently whenever I needed someone to listen.
- To my ancestors for all their values that were passed to me and your good deeds that inspire me in tough situations
- Finally, my country India that has given me privileges that helped me in living my American dream.

## **BIOGRAPHY**

Arjunsing Girase was born on July 31<sup>st</sup>, 1992, in the city of Dhule, Maharashtra, India. His father is an economics professor, and his mother is a housewife. His entire childhood was spent in the city of Nashik. He was raised with his elder brother Karan.

Arjun completed his undergraduate studies at the Institute of Chemical Technology, Mumbai. As a student in undergraduate, Arjun was involved in all the organizations of the colleges except his academia. He graduated in 2015 in Fiber and Textile Processing Technology. Post-graduation he worked as a research assistant in the same institute before joining NC State in fall 2016.

Arjun pursued his graduate studies in Textile Engineering as a Master's student and completed his thesis on carbon fiber heat sink structures in July 2018. Arjun began his doctorate at the Textile Protection and Comfort Center at NC State in August 2018 under the direction of Dr. Bryan Ormond and Dr. Donald Thompson. He will be graduating in December 2021.

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# **Chapter 1: Purpose and the Scope of Research**

## **1.1 Purpose**

Firefighting is one of the most noble professions in society. Unfortunately, this profession has been classified as “possibly carcinogenic” by the International Agency for Research on Cancer. This is because of the growing number of cancer incidences in the firefighting community.

Firefighters are exposed to a variety of chemicals that are present in the soot, smoke, and other chemicals that are present on the firegrounds. During a structural fire incident, various materials are burned that produce a variety of chemicals such as volatile organic compounds, polycyclic aromatic hydrocarbons (PAHs), phthalates, mineral particulates, etc [1]-[8]. These compounds may get deposited on the surface and migrate within the layers of the personal protective ensemble (PPE) of firefighters. Contaminants with low volatility can accumulate in the materials of the turnout gear and increase the risk to transfer to a firefighter’s skin during donning or doffing, on-scene decontamination, storage and cleaning. Since the contaminants may be present in such proximity to the skin determining the level of contamination of PPE is very important. A well-designed analytical method to determine the type of fireground contaminants is necessary.

The NFPA 1851 standard for selection, care and maintenance prescribed guidelines for washing PPE that are being followed by many independent service providers (ISPs) and fire departments are not very effective in removing all the contaminants [9]-[12]. The standard does not provide any criteria for screening the surfactants that are available in the industry. Certain factors limit the removal of contaminants such as the construction of thermal liners which are inherently open, porous fibrous structures with high surface areas that can entrap particles and

other contaminants. The shell materials typically contain aramid fibers that are sensitive to oxidation thus eliminating the use of effective hypochlorites or peroxidases in the cleaning process. Moisture barriers can limit the mobility of water in cleaning [13]. These constraints make the washing procedures less robust. It is crucial that the research be focused on evaluating and advancing the current methodologies that will help in cleaning the ensembles effectively.

The following research plan involves a series of steps that include : (1) identification of the fireground contaminants, (2) development of analytical methods to perform qualitative and quantitative analysis of these contaminants, (3) an in-depth evaluation of the cleaning methodologies practiced by the firefighting community and potential improvements for the same.

## **1.2 *Research Objectives***

### *1.2.1 Development of analytical procedures*

Numerous studies have been published confirming the presence of particulates, minerals, and, more importantly, PAHs, phthalates, and phenols as contaminants on structural suits after exposure to fires. A single analytical technique to simultaneously measure these chemicals of interest is not found in the current literature review. Thus, the first step will be to recognize what chemical compounds are frequently found in structural fires. From the literature, the classes of chemicals that should be focused on are PAHs, phenols and phthalates. Although the list of the fireground contaminants varies because different materials get burnt in structural fires, a standard mix consisting of targeted contaminants: phthalates, phenols, PAHs can be used to standardize an analytical method. The compounds in the mix will represent a class of chemicals to which they belong. A mix containing chemicals that are found in the gear as well as having higher toxicity that includes carcinogenic, probably carcinogenic, possibly carcinogenic will be given priority. Various methods from EPA are available to analyze phenols, phthalates and PAHs

separately using GC-MS. Thus, developing a single method to analyze these toxicants from the mix using the GC-MS technique is possible and of utmost importance. The retention times and calibration curves based on the peak responses will help in identifying and measuring the chemicals of interest.

To analyze the contamination in the materials pressurized solvent extraction (PSE) technique using Buchi speed extractor E-916 will be used. The PSE provides much higher efficiency, consumes less solvent and time as compared to traditional Soxhlet extractions that can take hours to finish the extraction. Hence solvent extraction methodologies can be developed by using materials spiked with a known concentration of the chemicals of interest and placing them into the stainless-steel cells. The increased pressure, elevated temperatures will help in improving the extraction of chemicals (present on the surface as well as inside the material) from the samples. This developed method will be beneficial in analyzing the contaminants from the actual samples taken from the retired gears given by various fire departments. Various fire departments have offered to support the project with retired gears. This not only will help us in the investigation of chemicals but also in our subsequent tasks that include testing and improving the washing procedures.

#### *1.2.2 Measurement of current washing procedures according to NFPA 1851 standard:*

The NFPA 1851 standard (2014 edition) for selection, care and maintenance has given the set of guidelines for routine cleaning. These cleaning guidelines have been followed by many ISPs and in the cleaning studies conducted by the NFPA's FPRF. The results indicated that the protocols that most departments and ISPs follow are not very effective at removing contaminants [14]. Limited research has been conducted to determine the decontamination efficiency of the washing techniques as per the NFPA 1851 standard [9]-[11]. Most of these studies have used

retired gears or samples from fire suppression training. Wipe sampling was mostly used to collect the contaminants from the PPE instead of using actual samples. Since there is no uniform contamination (qualitatively and quantitatively) and the collection of samples depends on the absorption efficiency of wipes used a thorough assessment of this extraction efficiency is not seen. This is a major research gap that can be seen in the research for evaluating the cleaning efficiency of the washing procedures according to the standard. Bench-scale level washing has been used in soil washing experiments to evaluate different surfactants to remove heavy metals, PAHs from soil samples [15]. A lab-scale evaluation of these washing procedures can help in studying the effects of washing parameters on cleaning efficiency. It will also help in testing the various products that are available in the market claiming “effective cleaning” of PPE. This single task will give us a comprehensive analysis of the standard procedures and help us in recognizing its limitations. A bench-scale analysis will also help in consuming fewer resources and it is always easy to control temperature, consumption of water on a bench-scale. A thorough analysis of washing parameters and their effects on cleaning efficiency is needed in this project. Initially, all the experiments will be performed on the outer-shell materials and then on the inner layers using the same procedure for all the tasks.

Our goal here is to establish a controlled washing procedure and analyze how standard guidelines for washing affect the removal of contaminants. It will help in assessing whether a single parameter affects a specific class of compounds more than the other. This includes taking uncontaminated swatches of size 5cm x 5cm of outer-shell materials. Control contamination will be performed on these samples with the known quantity using a repeater pipette. All these contaminated samples will be washed using a water shaking bath at 40°C and then analyzed using PSE and GC-MS. This will help in determining the cleaning efficiency. The NFPA 1851

standard has stated 40°C as the maximum washing temperature. Thus, a standard procedure for measuring the cleaning efficiency of any surfactant in a temperature-controlled environment is needed. Initially, we will use the commercial surfactants that are popular among the firefighting community.

On a pilot scale, we will use UNIMAC® 45 lbs washer extractor. The swatches will be contaminated using a known concentration and stitched onto the uncontaminated jackets. These jackets will be washed in the UNIMAC® and the swatches will be removed from the jackets and analyzed again using the analytical procedure. These results will be used as reference points for baseline comparison with the washing of the retired gears in UNIMAC®.

### *1.2.3 Laboratory studies for improving the cleaning efficiency*

This task involves studying the effects of variation in the parameters on the cleaning efficiency. This will also include investigating potential routes for decontamination. Chapter 7 in the NFPA 1851 standard has clearly stated the constraints for washing that includes temperature <105°F(40°C), G-force <100, 6.0 <pH<10.5, no use of chlorine bleaching agents. The washing efficiency can be improved by modifying the current washing procedures. All of the modifications will be tested on the bench-scale level using a water-shaking bath. Similar to the previous task, controlled contamination will be performed on the samples of outer-shell materials and washed on a water-shaking bath followed by analysis using PSE and GC-MS. The design of experiments will include modifications such as changing the temperature, longer washing durations, different surfactants. All of the experiments will be done in triplicates. The commercial surfactants that are popular in the firefighting community will be used initially. The effects of individual parameters on the washing efficiency will be studied. When all the results from the above modifications will be analyzed we will simulate these procedures on a full-scale

washer-extractor to see what are the deviations in upscaling the experiments. This will provide a thorough understanding of how well the bench-scale washing experiments replicate full-scale washing experiments.

This analysis will also help in establishing a relation between different washing parameters and individual compounds from the mix. Introducing new surfactants that are being developed will be obtained from the surfactant manufacturer. Microbial decontamination is a novel approach and will be studied in bench-scale washing experiments. Thus, the effect of adding microbes such as bacteria and fungi on improving decontamination will be studied. The best possible modifications that will demonstrate high washing efficiency will be further used on the real-world samples.

Liquid CO<sub>2</sub> cleaning has been investigated as a substitute for conventional dry cleaning. D. Aslanidou has explored the pathogenic decontamination of textiles using pressurized CO<sub>2</sub> [16]. Similar to the previous studies, swatches of known concentrations will be stitched on the jackets and washed with liquid CO<sub>2</sub>. A controlled contamination study will help in determining the efficacy of this method, and physical testing of the samples will be performed to investigate its effects on the durability of the gear. The retired gears will also be washed with liquid CO<sub>2</sub>. An experimental design will be performed on the retired gears which will include cutting a retired gear into 2 parts. The left part will be washed with the standard NFPA 1851 washing procedure and the right part with liquid CO<sub>2</sub> cleaning. Swatches will be cut before washing in triplicates from the respective parts and again after washing. The post-washed swatches will be taken from the adjacent sites of the pre-washed swatches. This will ensure that even though the contamination across the gear is non-uniform a direct comparison from adjacent sites will reduce the disparity in results. Similar to the conventional standard washing, modified washing



procedures that have proven to be effective in the previous phase will also be used in the experimental design. This experimental design will provide us with an unbiased evaluation of all the various washing techniques that will be developed.

The final phase of the project will include studying the impact of various washing techniques on the durability of the outershell and its accessories. The swatches of larger size (26 inch X 26 inch) will be prepared and accessories such as reflective trim, product labels will be attached. These swatches will be subjected to multiple washing using a particular technique. After washing, various tests will be performed and the results will be compared with the controlled sample. These include tearing strength, breaking strength, water repellency, reflectivity and visual inspection.

The physical testing of the samples is an important part of the project and will be performed in the final phase of this task. All the required test procedures that have been prescribed in chapter 12 of the NFPA 1851 standard will be performed.

## **Chapter 2:Introduction to Firefighting**

The job of a firefighter is exciting and dangerous. The unpredictable nature of fire, the external factors such as winds, burning of various materials producing different toxic chemicals make firefighter's jobs difficult and hazardous. "Constant vigilance" is the mantra of the firefighting community. Organized firefighting or community firefighting dates back to the Roman Empire during the reign of Augustus when the "watchmen" patrolled the streets of the city [17]. There is also evidence of using firefighting machinery in Egypt during the 3<sup>rd</sup> century BCE [13]. The first wardens appeared in North America in the 1600s. The volunteer fire service was organized by Benjamin franklin in 1736 [18].

### ***2.1 Current protection used by firefighters***

The firefighters' protective ensemble is the last line of defense and thus it is very imperative from the safety perspective. The firefighting profession includes tackling thermal hazards along with chemical and biological hazards. In 2018, 64 US firefighters died on duty, of which 13 died in structural fires [19]. Hence, it is very important to strike a balance between protective performance and comfort to facilitate a firefighter's duty. The durability of protective equipment is also an important factor that needs to be considered. Thus, the National Fire Protection Association (NFPA) standard for the selection, care, and maintenance (NFPA 1851) plays a vital role in navigating the firefighting community in taking care of the personal protective equipment (PPE).

NFPA 1971 Standard on Protective Ensembles for Structural Firefighting and Proximity Firefighting, 2018 edition defined structural firefighting ensembles as multiple elements of compliant protective clothing and equipment that when worn together provide protection [20]. Thus, the coverall includes: the coat, trouser, and elements include helmets, hoods, gloves, self-

contained breathing apparatus (SCBA), boots as shown in Figure 2-1[20]. The coat and trousers consist of three layers Figure 2-2 that include a durable outer shell that protects from abrasion. The outer shell durability is often considered as a parameter with overall gear performance and is the first line of defense. A moisture barrier that is an engineered membrane includes a thin film that is laminated on the woven or non-woven substrate that prevents liquid penetration. The third layer is a thermal liner that provides thermal insulation. The thermal liners are constructed using a woven face cloth and non-woven batt. The batt has air gaps that provide insulation and the face cloth acts as a wicking agent to move perspiration away from the body [21]. The thermal liner and moisture barrier together comprise 75% of the garment [22] [21] [23]. Detailed descriptions of these three layers and the materials used are provided in Figure 2-2:*Three layers of the garment*. [25]

Table 2-1. A leading manufacturer of aramid materials is DuPont®. The fabric has a meta-aramid chemical structure is known as Nomex® and para-aramid is called Kevlar®. Kevlar® has extraordinary strength, approximately five times the strength of steel, and Nomex® has a unique property of forming a protective char that will remain supple until it cools and will not melt or drip [21].

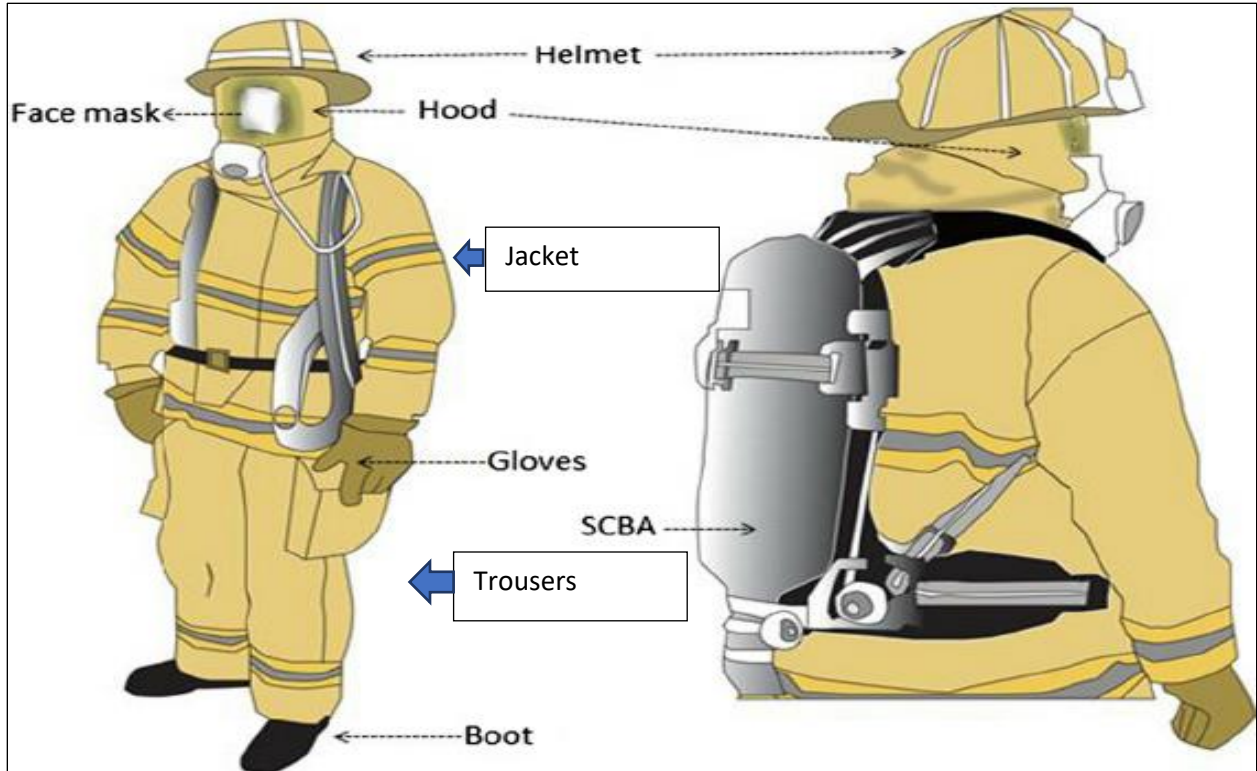


Figure 2-1: Personal Protective equipment. [24]

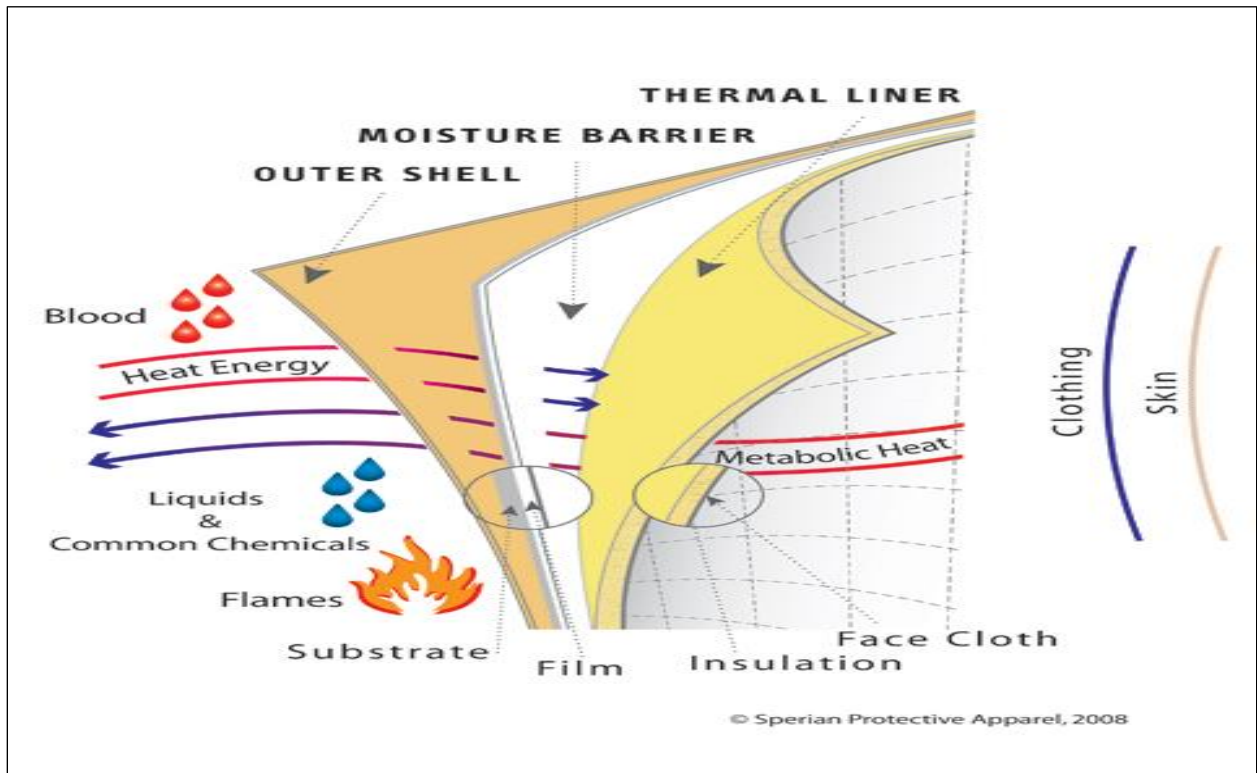


Figure 2-2: Three layers of the garment. [25]

Table 2-1: Turnout gear components, descriptions, materials used, and governing sections in NFPA 1971. [20]

<b>Layer</b>	<b>Governing NFPA 1971 sections</b>	<b>Purpose</b>	<b>Materials used</b>
<b>Outer shell</b>	3.3, 6.1, 7.1	Abrasion, cut resistance, flame protection	Polybenzimidazole (PBI), Nomex <sup>®</sup> , Kevlar <sup>®</sup> , polybenzoxazole (PBO)
<b>Moisture barrier</b>	3.3, 6.1, 7.1	Protection from water, chemicals, allows perspiration and breathability	Substrate: PBI, FR rayon, Nomex <sup>®</sup> , Kevlar <sup>®</sup> Film: polytetrafluoroethylene (PTFE), polyurethane (PU)
<b>Thermal liner</b>	3.3, 6.1, 7.1	Thermal protection from ambient heat	Polyimide, PBI, FR rayon, Nomex <sup>®</sup> , Kevlar <sup>®</sup>

## 2.2 Care and Maintenance of the gear

The NFPA 1851 standard has prescribed guidelines for the care and maintenance of the equipment. The outer shells and inner liners are washed separately for advanced cleaning. Advanced cleaning is performed by the independent service provider (ISPs) or manufacturer trained organization. For advanced cleaning, the temperature of washing should not exceed 105°F (40°C). The G-force should be less than 100 G and the pH of the detergent should be between 6-10.5. The washing detergent should not contain chlorine or oxidizing agents as oxidation can damage the aramid fibers of the outer shell. The washed ensembles should not be exposed to sunlight, as prolonged exposure can damage the aramid fibers in the outer shell. The washed ensembles are hung in the station for air drying. The moisture barrier promotes splash and sprays resistance that limits water mobility during cleaning. All these conditions make NFPA 1851 recommended washing procedure less robust. This is one of the possible reasons for

low decontamination efficiency [21] [14]. The advanced cleaning is performed by ISPs and manufacturer-trained organizations. Thus, different ISPs have a different approach in cleaning that includes the variation in the parameters such as washing durations, proprietary surfactants, temperature, etc. Hence, there is still a clear requirement of the standard method for the evaluation of the cleaning techniques.

### ***2.3 Decontamination studies review***

During firefighting, firefighters are exposed to numerous chemicals. Structural fires contain combustion products from burning furniture, carpet, and other synthetic materials. This results in the emission of PAHs and volatile organic compounds. These chemicals pose a major threat to the health of firefighters. Thus, the efficacy of decontamination is of primal importance in protecting the firefighting community. A very limited number of studies have been conducted on evaluating the decontamination efficiency of the firefighters' gear. While all the researchers agree that structural fires can contain numerous compounds, many studies have been focused mainly on the removal of PAHs.

The interim report in 2017 [12] and the article labeled as "*How Clean is Clean?*" in the "Fire Engineering" magazine January 2018 edition by Mr. Jeffrey Stull shed light on the inefficacy of the laundering processes in the firefighting community. Since then, various research institutes are working on improving the laundering process, although the research is still in an infant stage. The currently employed washing procedures remove less than 40% of toxins from the gears [12]. These residual contaminants after chronic exposure to the skin can be harmful to firefighters. Kenneth Fent studied the impact of laundering PPE to reduce exposure to chemicals such as flame retardants and PAHs on hoods. The results indicated (56-81)% lower levels of contamination than the unlaundered hoods. With the unlaundered hoods, another set of heavily

exposed hoods, and unused (new) hoods were washed together, they found elevated levels of the contaminants in the unused and first set of unlaundered hoods indicating cross-contamination [9].

A comparative study of three different on-site decontamination techniques was performed by Fent and colleagues: dry brushing, air-drying, and commercial dish wash soap (10 mL in two gallons of water). The gears were used in simulated firefighting scenarios and then were decontaminated. The dry brush technique removed 24% of the contaminants, washing with a dish soap decreased the contamination by 85%. The air-drying technique increased the contamination by 0.5% which was concluded as an experimental artifact. Although, the wet decontamination indicated high PAH removal, one of the limitations of the study was that using wipes to collect PAHs from the gear and not using actual samples from the gear. This greatly affected the collected data since the levels of contamination (both pre-decon and post-decon) depended heavily on the absorbing efficacy of the wipes used [11]. A study on water-only decontamination resulted in an overall increase of 42% in contamination. The water-only decontamination technique included placing the legacy turnout gears on the ground and rinsing it with a gardening hose. The study concluded with an increase in the overall level of contamination which was due to the spatial variability in contamination in different locations [10]. This study highlighted the need for surface-active agents along with brushing in wet decontamination techniques to remove the particles from the surface.

The assessment studies discussed above highlight a lack of uniform contamination. All of these studies have used simulated structural fires as the primary source of contamination that limits the thorough analysis of the fireground contaminants. The use of simulated structural fires to provide exposure to chemicals is not a repeatable method of contamination. Also, the cost of

having structural fires as the source of contamination is very high that limits the practicality of the experiment. While one part of the gear may be heavily exposed to the smoke, the other part may not have the same level of exposure. This will inhibit a uniform sampling for the assessment. As discussed above, using actual samples from the gear instead of wipe samples will provide a more thorough understanding of the contamination dislodged inside the fabric.

All of these indicate a need for a repeatable and reproducible lab-scale contamination and analysis procedure. The studies also fail to explain the relationship between different washing parameters and the removal of contaminants. A uniform level of contamination and washing of the garments in a controlled environment is critical to gaining an understanding of the different washing parameters.

#### ***2.4 Dirty Gear: A badge of honor?***

“Every firefighter remembers his/her first shift. You aren’t sure what to do, so you become a casual observer and follow the lead of grizzled veterans. The seasoned firefighters will tell you: dirty gear is the sign of a real firefighter. The difficult part for a rookie firefighter is to learn to separate veterans’ wisdom with their bad habits”-

This was written in the article by Paul Wayne Powell nearly a decade ago (August 1<sup>st</sup> 2004) [23]. This article highlights the importance of a cultural change in the fire service. Many surveys and studies have been focused on the fact that the management of the culture affects the firefighting practice. A cultural organization consists of values that directly affect the occupational practice thus highlighting the importance of informal communication along with formal communication [26]. The firefighting organizations are the modern era knighthood communities with all the discipline, values, sense of duty inculcated in them. The tangibles like dirty gear carry a sense of machismo indicating reliability, expertise, and professional



competence. Gear is perceived as a symbol that goes beyond superficial appearance and not a tool. However, the increased awareness about the risk of cancer in the firefighting profession has highlighted the problems associated with dirty gear. Thus, a slow shift in the perception and attitude is seen in the firefighting community [27]. The Palm Beach County Fire Rescue (PBCFR) case study of 2017 consisted of 1500 firefighters. This study conducted a survey and it highlighted some interesting key points [27]:

- Historically 80% of firefighters perceived dirty gear as the badge of honor. The senior firefighters (more than 5 years of service) had this belief. The seasoned firefighters even stated that before the establishment of the “mandatory annual cleaning of the gear” rule, many of them never washed the gear. However, the majority of the young firefighters (less than 5 years of service) acknowledge that the dirty gear is problematic.
- Establishing a discipline of cleaning at the training centers so the new generation will already be a part of this new regime
- Change from the top is equally important

Gross field decontamination: Although incorporating gross field decontamination is very important, several firefighters expressed their concerns. It included wearing wet protective ensembles for consecutive calls for fire rescue. They feared that wearing a wet ensemble for the second call for firefighting might “steam” them. Another concern was the lack of mobility and discomfort due to wet gears. The research team also noticed a lack of belief about the efficacy of gross field decontamination.

The lack of time for cleaning: Some busy stations cover 15-20 calls a day and this puts a heavy toll on the firefighters. The need for the short-term goal to take a rest and be sharp for the

next call dominates the long-term goal of cleaning and reducing potential exposures. Thus, finding a balance between both goals is very important.

The model of change is shown in Figure 2-3. The model indicates the complexities involved in changing the culture. Thus, the efforts of both organizations and individuals are needed in shifting the culture and incorporating the new practices.

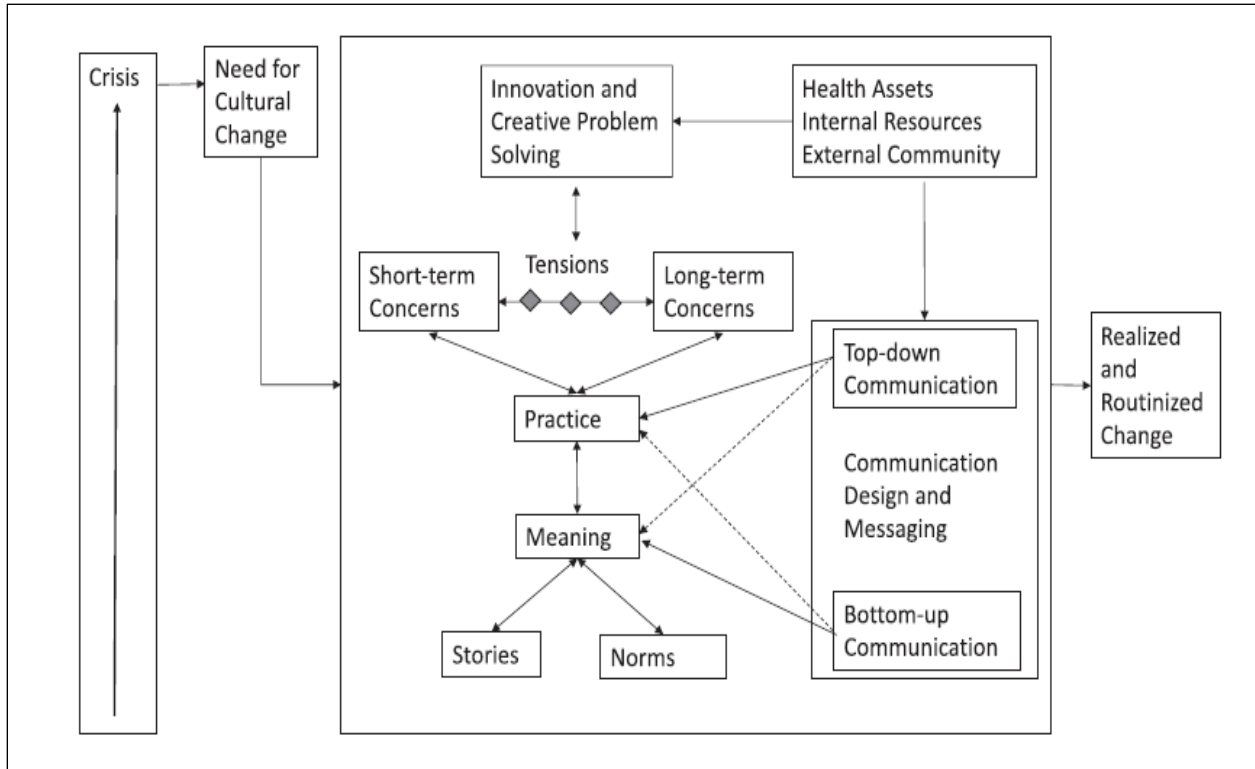


Figure 2-3: Model of change processes. [27]

In an intervention study conducted in two fire departments of Florida, the primary focus was on changing the perception towards cleaning. The study used the Integrated Model of Behavioral Prediction that assumes human beings are rational actors. According to this model, three determinants significantly predict behavioral intention: attitude, perceived norms and self-efficacy. This study included 226 firefighters and the intervention process was focused primarily on informing the firefighters about the risk of cancer, overcoming barriers in decontamination,

cultural change, etc. The study resulted in increasing firefighters' intention to engage in decontamination behavior [28].

For a firefighter, his/her gear is a very personal thing. It is infused with memories, values, and experiences but it is also unwise to not perceive it as a tool and the only protection during the face of adversity.

Thus, it is very important to take proper care of the PPE. The NFPA 1851 standard is also revising the guidelines of washing to fill the research gaps, address the efficacy of removing contaminants, and make washing and decontamination procedures less cumbersome and more economical.

## Chapter 3: Fireground Contaminants

Modern furnishings today are composed of various artificial materials, which release harmful compounds during combustion. During structural firefighting, firefighters are exposed to the released compounds from combustion. Over the years, exposure studies have been performed to assess the toxicity and its effects on firefighters. Until the 1980s, a limited number of studies were performed on residential fire exposure. Detection of the chemicals in older studies was limited due to technological constraints and mainly focused on the detection of carbon monoxides. Since then, the chemicals detected have expanded to compounds such as hydrogen cyanides, formaldehyde, carbon monoxides, and dichlorofluoromethane. Some of the important highlights included: (1) Intensity of the fire did affect the concentration of the gases. (2) Readings obtained were compared with the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit values (TLV). TLV included –(a) Short term exposure limits (STEL), (b) Immediately dangerous to life and health (IDLH) levels, (c) Short term lethal concentration (STLC) levels. Carbon monoxide exceeded STEL values. (3) The intensity of the smoke did not indicate the levels of toxicity which was a general perception at that time. The perception of low exposure equates to lower toxicity has resulted in worse exposures in some cases as a personal protective ensemble not being worn properly [1], [2]. Toxic air contaminants such as carbon monoxide, respirable particles, and VOCs are present in both gaseous and particle phases from burning bush fires. Such contaminants have both short-term and long-term adverse effects [29].

Juha performed a study to assess multi-route exposure in firefighters' suits. Both conventional and modern simulators were used in this assessment. The conventional simulator was a large block of flat (three concrete made floors) that used chipboard, conifer plywood, or

pure spruce wood as fuel while the modern simulator was made from metal and had been built on two separate floors that used propane as burning material and smoke was made with the help of a generator using mineral oil. Six polycyclic aromatic hydrocarbons (PAHs) and five volatile organic compounds (VOCs) were collected from a conventional simulator and two PAHs and two VOCs were collected from a modern simulator. The urine samples indicated dermal exposure was the prominent mode of exposure [3]. Smoke particles in the ultrafine range indicated risks for cardiovascular diseases and possible association with lung cancer [5], [30].

Firefighters are exposed to fine particulate matter (2.5 $\mu$ m diameter or less) and sub-micron particles during overhaul activities and in the firehouse. Analysis of residential and vehicle fires highlighted that structural firefighters were exposed to a high number of sub-micron particles along with traces of PAHs such as naphthalene, benzofluoranthene and acenaphthylene suggesting dermal absorption as a potential route of exposure [8]. Assessment of California firefighters' blood concentration for selected chemicals showed that six participants had higher concentrations of mercury in their blood than the threshold value of 10  $\mu$ g/L reported by the National Health and Nutrition Examination Survey (NHANES) [31].

As the consumption of artificial materials increases, structural fires emit a variety of toxic compounds such as PAHs, phthalates, and phenols. Partial or complete combustion of the household polymers release the VOCs. Structural fires are a primary contributor to occupational exposure to PAHs which results in promoting cardiovascular illness in the firefighting community. Various studies have quantified the concentrations of PAHs in smoke in both simulated fire incidents and real fire incidents. Because self-contained breathing apparatus (SCBA) inhibits exposure via inhalation when used appropriately, dermal exposure is an important route of exposure, which is proven through wipes and other swabs taken from turnout

suits [6] [8] [32] [33]. A single training session demonstrated the deposition of benzo[a]pyrene on the outer shells of personal protective equipment (PPE) with a high range of 12 to 157  $\mu\text{g}/\text{m}^2$ . This amount of deposition could have potentially chronic effects on the health of firefighters [34]. Oliviera assessed six mono hydroxyl metabolites (OH-PAH) in the post-shift urine of around 153 wildland firefighters. Overall median levels suggested an increase in PAH levels in exposed firefighters by 1.7-35 times than non-exposed ones [35]. Several studies have found PAHs in the urine samples of firefighters as biomarkers [7] [35] [30] [36].

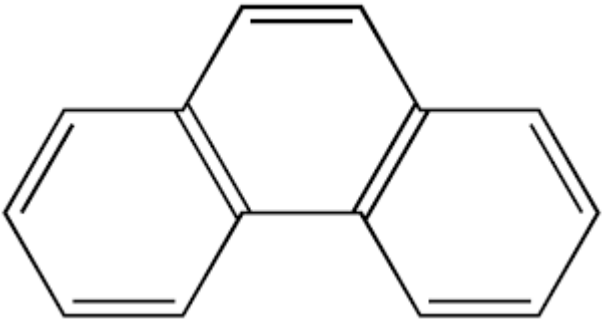
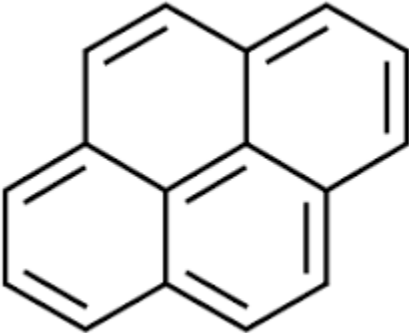
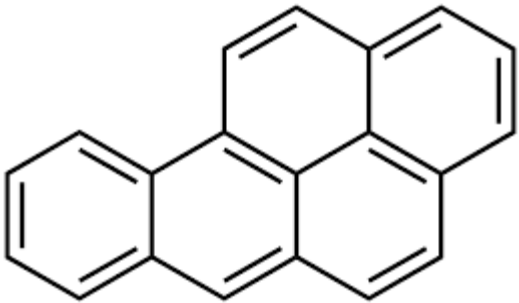
The Stockholm study suggested that firefighters have elevated levels of stomach cancer than the general population. The cohort study included 1080 men who worked at least 1 year as a firefighter in the city of Stockholm. The employment and cancer-related information was obtained through official records and National Cancer Register respectively. All first-time cancer for each specific cancer site were included that indicated a relationship between increasing the risk of cancer with longer employment duration. The potential reason stated for the increased risk was chemical exposure at work although the data on the number of fires fought was not available. In addition to chemical exposure, most firefighters work in shifts that disrupts the circadian rhythm and potentially increase the health risk [37].

All of the above studies indicate different classes of chemicals. These chemicals are the by-products of the combustion of various compounds. Majorly found are polycyclic aromatic hydrocarbons, phthalates and phenols [35] [38]. To decontaminate PPE from such carcinogenic compounds it is important to understand the fundamental properties of such organic compounds. Owing to their different chemical natures it is important to classify them separately and study their availability in the environment and their removal.

### 3.1 *Polycyclic aromatic hydrocarbons*

Polycyclic aromatic hydrocarbons (PAH) are a broad category of persistent organic pollutants that are constituted by a large number of individual substances. PAHs have two or more single or fused aromatic rings. Small PAHs contain up to six fused aromatic rings and large PAHs have more than six fused aromatic rings [39]. The US Environmental Protection Agency (EPA) has identified 16 priority PAHs due to their toxicity: naphthalene, acenaphthylene, acenaphthene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, chrysene, dibenzo[ah]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, pyrene, phenanthrene. Some of the PAHs that have been used in the analysis further in the research are shown in Table 3-1.

Table 3-1: Selected properties of PAHs. [39]

Compounds	Boiling point(°C)	Structures
Phenanthrene	218	
Pyrene	404	
Benzo[a]pyrene	495	

### 3.1.1 Physical and chemical properties

PAHs generally have high melting and boiling points, low vapor pressure, and generally low aqueous solubility. As the molecular weight increases, a general trend of decreasing vapor pressure is observed in Figure 3-1. Also, higher ring compounds show resistance to oxidation and reduction. With every additional ring in PAHs, there is a decrease in aqueous solubility.



PAHs are highly lipophilic and soluble in organic solvents. PAHs have a unique identification UV absorbance spectrum, which is helpful in their identification [40] [41].

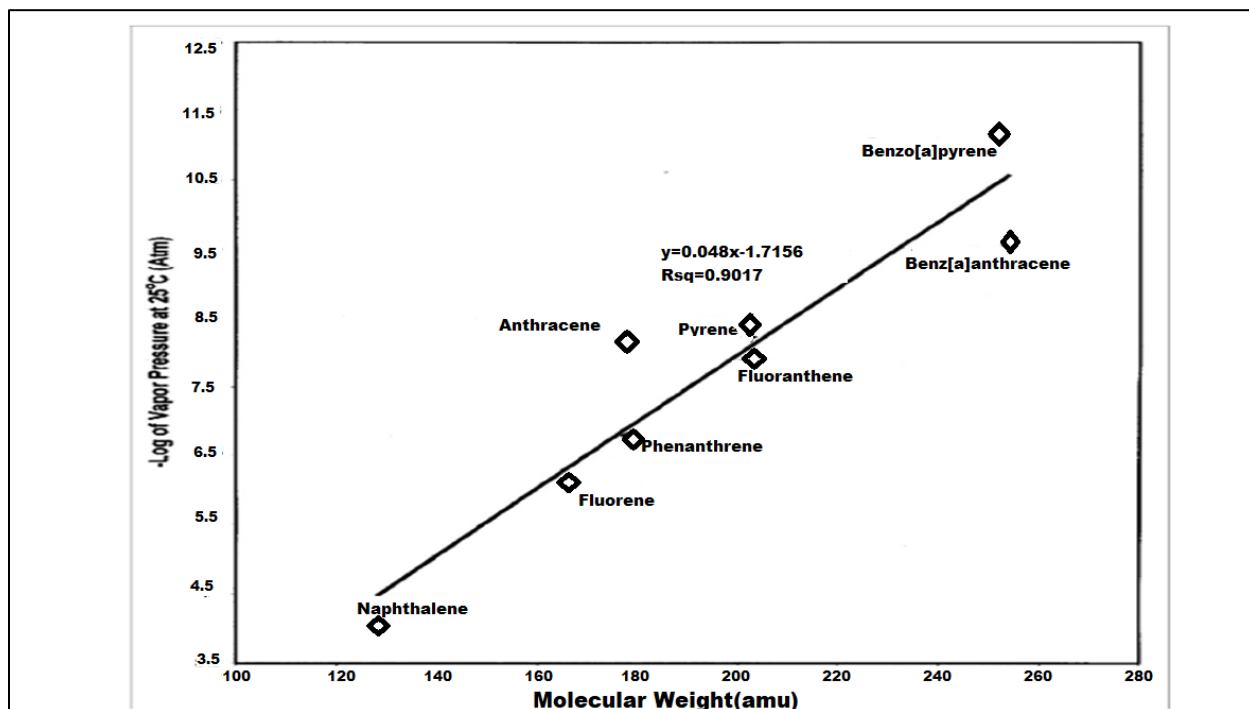


Figure 3-1: Relationship between vapor pressure and molecular weights of PAHs.[41]

### 3.1.2 Emission of PAHs

Incomplete combustion of organic matter produces PAHs in the environment. Anthropogenic sources such as agricultural fires, fuel combustion, power plants, and other industrial sources contribute heavily to the generation of PAHs along with natural sources such as volcanoes, wildfires, etc. PAHs can be formed naturally by low-temperature, high-pressure reactions of natural organic matter [42].

PAHs exist in the vapor phase and solid phase after they are released into the atmosphere. Due to low vapor pressure, PAHs are easily adsorbed onto the surface of particulate matter. One of the studies conducted by the Electric Power Research Institute concluded there is a difference between PAH concentrations for the vapor phase ( $741 \text{ ng/m}^3$ ) which is higher than the concentration in particulate phases ( $12 \text{ ng/m}^3$ ). The lower molecular weight and higher vapor

pressure PAHs exist in the vapor phase while lower vapor pressure and higher molecular weight PAHs exist in the particulate phase [43]. PAHs concentration in the particulate phase also has a significant relationship with the amount of dust present in the atmospheric air. Thus, the concentration of PAHs in the gas phase is higher in summer and tropical regions while in winter and arctic regions, the particulate phase PAHs have higher concentrations [40] [42]

### *3.1.3 Surface deposition of PAHs*

PAHs are continuously deposited on the earth's surface due to wet or dry deposition. PAHs adsorption on the soil depends on the properties of the soil and PAHs. This governs the soil mobility of the PAHs. The octanol-water partitioning coefficient ( $K_{OW}$ ) is an important factor in determining the adsorption on soils which quantifies the solubility of an organic compound in water. Detail explanation of the  $K_{OW}$  is provided in the next chapter in section 4.9. An increase in  $K_{OW}$  indicates a decrease in aqueous solubility and adsorption tendency on the soil for PAHs increases. Similarly, atmospheric particles can settle on different water surfaces where they are integrated with the sediments. Non-polar structures of PAHs reduce aqueous solubility and immobilize them due to their attachments to sediments [41].

### *3.1.4 Toxicity of PAHs*

Occupational exposures to PAHs for workers working in mining, coal industry, mechanics, and oil refining can occur by breathing the fumes generated in the respective work through routes of exposure such as inhalation, ingestion, and dermal. Thus, the acute effects of PAHs depend on the duration of exposure, concentration, and route of exposure. Short-term effects include asthmatic and thrombotic effects [44]. Laboratory tests on animals have found that long-term exposures to PAHs can result in cancer, liver damage, and adverse reproductive effects. Frequent dermal exposure to naphthalene showed redness and swelling of the skin.

Inhalation and ingestion have been shown to decrease red blood cells count. DNA damage has been reported in various studies. Reactive metabolites of some PAHs bind to cellular proteins and DNA that disrupt the biochemical properties and cause mutations [44] [45] [46].

### *3.1.5 Removal of PAHs*

Several methods have been used to remove PAHs from the environment that includes conventional processes such as ozonation, photolysis, and some developed recently such as chemical degradation, biodegradation, ultrasonication, and sorption process using super adsorbers.

#### *3.1.5.1 Biodegradation*

Biodegradation of PAHs can happen via both aerobic and anaerobic modes. When PAHs are bioavailable, they are degraded by bacteria. To be available in the environment, PAHs need to be either in a dissolved state or vapor phase [41]. The bioavailability of PAHs is complicated since PAHs desorb from various surfaces at different rates due to different chemical structures. Freshly produced C-14 labeled chrysene and phenanthrene desorb from soils more rapidly as compared to chrysene and phenanthrene adsorbed on the soil for a longer time. Initially, PAHs desorb rapidly but the rate decreases rapidly over time. This is mainly due to a decrease in the concentration gradient as PAHs desorbed [47]. The solubility character of PAHs needs to be taken into consideration as it depends on the molecular weights. When individual PAHs reach the aqueous solubility, the concentration gradient between the sorbent and the aqueous phase decreases which slows down the desorption rate. Along with molecular weight, the structure of the compound is very vital in determining its reactivity. Angular ring structures have better thermodynamic stability than linear and clustered structures. Also, the open areas between the angular structures are more susceptible to enzyme attack hence these structures are more

biodegradable [41]. Bioremediation and biodegradation are being researched thoroughly due to their environmental and economic advantages. The fundamental difference is biodegradation can be a natural process, but bioremediation is an engineered process and faster than biodegradation. The PAH degrading microorganisms can be algae, fungi, and bacteria that transform the complex PAH structures into less complex metabolites. The rate of bioremediation depends on environmental conditions, nature, and structure of the chemical compound. The rate of biodegradation depends on pH, temperature, oxygen, microbial population, chemical structure of the compound, and cellular transport properties [48] [49]. All the microorganisms take a longer time (sometimes weeks) to process contaminants compared to other methods used to degrade the contaminants which is a major shortcoming for this method.

#### 3.1.5.1.1 *Bacteria*

Long-term petrochemical waste discharge contains bacteria that can degrade the PAH benzo[a]pyrene (BaP) to a considerable extent. *Sphingomonas paucimobilis* strain EPA 505 degraded BaP and decreased the concentration by 5% after incubating for 168 hours [50]. Cultures of *Mycobacterium vanbaalenii* metabolized 15% benzo[a]anthracene in 12 days of incubation [51]. The contaminated sites such as oil, motor oil, refineries contained different strains that degraded phenanthrene. The species of *Pseudomonas*, *Agrobacterium*, *Bacillus*, *Burkholderia*, and *Spinghomonas* are primarily found strains in these sites [52].

#### 3.1.5.1.2 *Fungi*

In the class of fungi, lignolytic fungi have been intensively studied. The lignolytic fungi produce extracellular enzymes that have low substrate specificity and hence can degrade a variety of compounds. The lignolytic system has three main enzyme groups: lignin peroxidases, manganese-dependent *peroxidases*, and *phenoloxidases*. These enzymes have degraded PAHs

[53]. The variation in the degradation of PAHs varies with the types of enzymes. There have been a variety of different strains obtained from lignolytic fungi that degrade different PAHs, for example, strain 984 degraded naphthalene by around 69%, while strain 870 degraded naphthalene by 17% and strain 870 degraded phenanthrene by 12% [54]. Low molecular weight PAHs (2-3 rings) were degraded by *Aspergillus sp.*, *Trichocladium canadense* and *Fursarium oxysporum* [55].

#### 3.1.5.1.3 Algae

Marine algae such as cyanobacteria, green algae, and diatoms metabolize naphthalene to a series of metabolites. BaP is metabolized and transformed into diols by marine algae such as *Selenastrum capricornutum* that uses dioxygenase systems of enzyme to degrade BaP. Some algae need bacteria to enhance their metabolism for degrading PAHs. Some algae-bacteria microcosms have removed more than 85% PAHs in the presence of continuous lightings. The microalgal species that have the ability of accumulation along with degradation include *Nitzschia sp.* and *S.costatum*. [55]

#### 3.1.5.1.4 Enzymes

Oxygenase, dehydrogenase, and lignolytic are three prominent enzymes involved in the degradation of PAHs. The fungal producing lignolytic enzymes include manganese peroxidase, laccase, and lignin peroxidase that catalyze radical formation by oxidizing the PAHs [55,56]. Laccase and Mn-dependent peroxidase enzyme can be abundantly found in spent mushroom compost. Mushroom compost has been reported to degrade PAHs [56]. A research study devised a correlation of ionization potential with degradation of PAHs. The ionization potential (IP) was defined as the energy required to remove an electron from the bond to form a cationic radical. The IP values recorded for different PAHs are given in Table 3-2. The enzymes have different IP

values: *peroxidases* ( $IP \leq 7.35$  eV), *laccase* ( $IP \leq 7.45$  eV), *Mn-dependent peroxidase* ( $IP \leq 8.19$  eV) *ligninase* ( $IP \leq 7.55$  eV). These enzymes use a single-electron oxidation mechanism to degrade PAHs. Considering the different ionization potential values Mn-dependent peroxidase can certainly degrade PAHs which indicates the potential in inoculation techniques to incorporate surfactants to enhance solubility [57]. Most of the enzymes work efficiently between (20-45)°C. Extreme temperatures reduce the efficiency of laccase (30% at 5°C, 31% at 75°C) although the laccase from the fungus *Marasmius quercophilus* can operate at 80°C. Mn-peroxidases can work at higher temperatures. The lignolytic enzymes are not substrate-specific and they degrade PAHs as well as phenolic compounds by one-electron oxidation mechanism. Mn-peroxidases from fungi *Nematomola forwardi* degrades a variety of PAHs into carbon dioxide [55].

Table 3-2: PAHs: ionization potential values. [57]

PAHs	Ionization potential(eV)
Phenanthrene	8.03
Anthracene	7.43
Fluoranthene	7.90
Pyrene	7.53
Benzo[a]pyrene	7.21
Benzo[g,h,i]perylene	7.31
Chrysene	7.81

### 3.1.5.2 Photolysis degradation

Photolysis reactions occur when light is absorbed by PAH which excites the electrons making an unstable structure. This reaction is more effective when PAHs are in the vapor phase. In the particle phase, these reactions are more effective for larger particles due to the higher surface area available. Similar to biodegradation, the linear, 2-ring, and clustered structures degrade rapidly in photolysis [41]. Angular PAHs such as phenanthrene is the slowest to

degrade. Also, low molecular weight compounds such as naphthalene degrade faster due to photolysis [58].

#### *3.1.5.3 Chemical Degradation*

Chemical degradation is a conventional process in the removal of PAHs. It includes an oxidation mechanism using ozonation, chlorine, and potassium permanganate. The major drawback of using chemicals in degrading of PAHs is its reaction with the aquatic organic matter which creates further problems, for example, chlorine reacts with organic matter in water producing by-products that are carcinogenic halogenated hydrocarbons (trihalomethanes and haloacetic acids). Ozonation and direct photolysis are other techniques used in the oxidation process. Since NFPA 1851 document advises against oxidation/bleaching of PPE, discussion of this technique can be classified as out of scope for our research [59].

#### *3.1.5.4 Sorption*

The sorption process includes adsorption, absorption, and ion exchange mechanisms. The adsorption process includes mass transfer via substance accumulation at the interface of any two phases [60]. The constituents adsorbed are mainly responsible for removing the pollutants from water [61]. If the adsorption is caused by Van der Waals forces of attraction between the adsorbent and the surface it is considered as physisorption. The process can be reversible. When the adsorption involves chemical bonding between the adsorbed surfaces and the solid surface it is considered as chemisorption. Chemisorption is a monolayer process. Both processes can occur simultaneously when the conditions are favorable. During physical adsorption, there is a decrease in the free energy and entropy of the system. The sorption method is considered a better method in the removal of PAHs due to low investment and maintenance cost, simple design, no

by-product formation. Also, PAHs have low aqueous solubility and strong sorption affinity to the solid media thus sorption method has become a promising option [62].

#### *3.1.5.4.1 Sorption media*

##### *3.1.5.4.1.1 Activated carbon*

Activated carbon has a very high specific surface area that ranges from 300 m<sup>2</sup>/g to 3000 m<sup>2</sup>/g. Activated carbon is from carbonating various materials such as sewage sludge materials, petroleum coke, coal, etc. Thus, it is abundantly available which makes it an economical option. Activated carbon is prepared in the form of powder or granules and is commonly used in adsorption applications [60]. Various studies have been carried out to study the effects of activated carbon on PAH adsorption (Table 3-3) . With the small addition of powdered activated carbon in the contaminated PAHs solution, the experiments demonstrated PAHs removal efficiency by more than 90%. The adsorption efficiency of activated carbon can be modified by changing activation process parameters such as temperature, activating agent, and oxidant flow rate [60] [63] [64] [65].



Table 3-3: Various studies on activated carbon. [60] [63] [64] [65]

<b>Materials</b>	<b>Study</b>	<b>Result: PAH removal efficiency</b>
Powdered activated carbon	PAHs concentration (30mg/kg) with activated carbon (50mg) in 40mL solution shaken for 30 days	Phenathrene:95%, Anthracene:97.5% Pyrene:98% Benzo[a]pyrene: 88%
Activated carbon	12mg/L naphthalene and 1mg/L fluorene mixed with 50mg activated petroleum coke at 25°C for 15 mins	>97% Naphthalene >98% Fluorene
Granular activated carbon, powdered activated carbon	2% activated carbon to urban soil, the concentration of PAH 38mg/kg	99% Powdered carbon, 64% Granulated carbon
Powdered activated carbon, granulated activated carbon	2% activated carbon in PAH (31ng/L) contaminated water	93%: Powdered activated carbon 84%: Granulated activated carbon after 19 months

#### 3.1.5.4.1.2 Biochar

Biochar has favorable properties, like high surface area and porous structure, which makes it an excellent adsorbent. It is produced by pyrolysis of industrial residues, agricultural residues, and organic matter in the absence of oxygen at a temperature between 300 °C to 700 °C [60]. Biochar has been used in improving the soil properties by assisting in retaining nutrients and encouraging microbial activities [66]. The particle size of biochar does not have a significant effect on the sorption of PAHs [67]. However, it has been demonstrated that the sorption equilibrium for other compounds such as triazine can be achieved quickly by decreasing the

particle size. Biochar is composed of glassy and rubbery parts. The glassy part is categorized as non-linear competitive adsorption of organic contaminants while the rubbery section is associated with linear non-competitive partitioning of organic contaminants [68]. The adsorption process using biochar has many steps included: surface coverage, multilayer adsorption, condensation in capillary pores, adsorption into the polymeric matrix [60].

*Table 3-4: Studies on Biochar. [60] [69]*

<b>Materials</b>	<b>Study</b>	<b>Result</b>
Biochar	Phenanthrene: 9.07 mg/L, fluorene: 10.05mg/L, pyrene: 10.57 mg/L, 3 different biochars with different doses used that were pyrolyzed at different temperatures, 400°C (6g/L), 600 °C (6g/L) and 800°C (2g/L)	Biochar at 800°C: (95.8-98.6)%, Biochar at 600°C (82.4-93.4) Biochar at 400°C (71.8-88.1)
Biochar	5gm contaminated soil mixed with 10mL 1:1 acetone and hexane	>50% for high molecular weight PAHs >40% for low molecular weights PAHs
Activated carbon/biochar	0.5-10% activated carbon and biochar mixture. PAH concentration in sewage sludge:13.2 ng/L	56-95% for activated carbon 57% Biochar

#### *3.1.5.4.1.3 Modified clay mineral*

Clay minerals such as zeolite, bentonite, and sepiolite have been used to adsorb PAHs such as phenanthrene, pyrene, and benzo[a]pyrene. Organozeolite removed 98% fluorene, fluoranthene, and pyrene from a lab prepared solution of a mixture of PAHs using acetone. Zeolites don't shrink or swell, and their particle size is about a millimeter. These features make

them suitable for filtration systems [60]. Clay minerals are modified to improve the adsorption efficiency. The inorganic exchangeable cations are replaced by organic cations such as quaternary ammonium salt. These compounds have cationic heads and long hydrophobic molecules forming a surfactant [70] [71]. Cetyl pyridinium exchanged low-pH montmorillonite clay has been proven an effective adsorbent in cleaning groundwater from PAHs. Also, the synergistic effect of granular activated carbon and modified clay demonstrated better PAH removal efficiency. Some of the studies used cetyl pyridinium along with sand, resulting in a 90% removal efficiency of PAHs [60].

Thus, the additives such as biochar, clay minerals can improve the desorption of the PAHs from the fabric by providing them the adsorption sites that have a greater affinity.

#### *3.1.5.4.2 Factors affecting the adsorption process*

##### *3.1.5.4.2.1 Particle size and surface area*

The particle size and the adsorption capacity are inversely related [72]. The adsorption process is a surface phenomenon that depends on the specific surface area that is the fraction of the total surface area available for adsorption [73]. Many researchers have demonstrated that the smaller size of the adsorption media has a large surface area for high mass transfer that results in high adsorption capacity [60].

##### *3.1.5.4.2.2 Solubility*

The extent of adsorption of the solute and the solubility of the solute are inversely proportional. Also, there is an inverse relationship between the molecular weight of PAHs and the solubility of PAHs such as naphthalene, acenaphthylene, and phenanthrene [60].

#### 3.1.5.4.2.3 Salinity

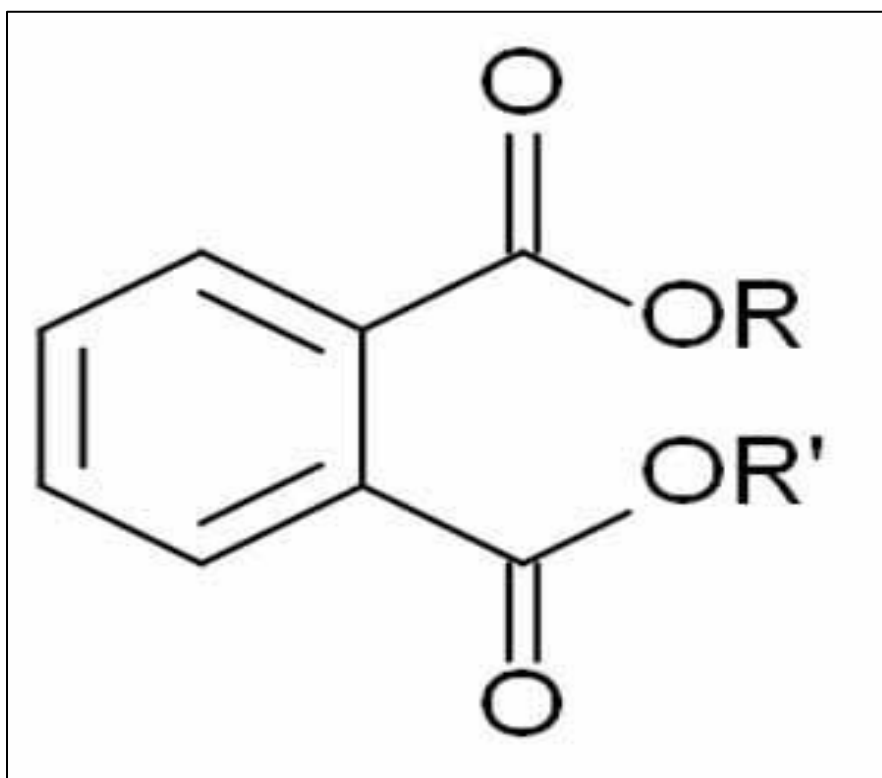
Increasing the salinity of the solution increases PAHs adsorption capacity. Ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , bind with water molecules tightly into hydration shells which reduces the water solubility of PAHs along with the cavity volume to accommodate organic solutes that force PAHs to get adsorbed on the surface ultimately increasing the adsorption [74]. In a comparative study, the adsorption coefficient for phenanthrene increased by 15% in the KCl solution as compared to the coefficient in water. Increasing the NaCl concentration in an aqueous solution increased the adsorption of phenanthrene. Thus, the hardness of water may affect the removal of PAHs.

The pH of the solution affects the distribution of the surface charge of the adsorbent affecting the extent of adsorption. The phenanthrene demonstrated maximum adsorption of greater than 90% for pH 2 and the basic pH decreased to 40%. For acidic pH, higher positive ions interacted with phenanthrene molecules which improved the adsorption while for alkaline pH the  $\text{OH}^-$  ions attacked the adsorption sites which decreased the overall adsorption. Similarly, naphthalene showed higher adsorption at pH 2 as compared to the alkaline pH [60]. This highlighted the importance of the pH of the surfactant in removing PAHs. The surfactant PAHs used in washing the PPE needs to be in the range of 6 to 10.5. Thus, keeping the pH of the detergent on the slightly acidic side may help in improving the PAHs removal. Also, a detailed analysis of the surfactant chemistry with PAHs along with its impact on the physical properties of the outershell need to be investigated

### 3.2 Phthalates

Phthalates are the esters of phthalic acids (Figure 3-2) which are widely used as plasticizers that are added to impart flexibility to polymers. Low volatility and chemically stable

structure make them ideal to be used as plasticizers. Phthalates are classified into low and high molecular weights which can be used accordingly in end-user applications. High molecular weight compounds have 9 to 13 carbon atoms which increase their structural robustness and durability. This makes them suitable to be used in PVC for making pipes, flooring, roofing, etc. Low molecular weight compounds consist of 3 to 8 carbon atoms such as di-ethyl-hexyl-phthalates (DEHP) and di-butyl phthalates (DBP). They are used in inks, cosmetics, medical devices. DEHP is one of the predominant plasticizers with a production volume of 3-4 million tons worldwide [75] [76].



*Figure 3-2: Structure of phthalates.*

### *3.2.1 Physical and chemical properties*

Phthalates vary greatly in structures that result in a wide range of physical and chemical properties. This wide range of properties is mainly due to different alkyl chain lengths substituted on diester groups. Different chemical properties such as vapor pressure, octanol-

water partition coefficient, and solubility in water are affected by the structures of phthalates. Phthalates are present in a liquid state at room temperature. The melting point of phthalates lie generally between  $-58^{\circ}\text{C}$  to  $5^{\circ}\text{C}$  and boiling points range from  $230^{\circ}\text{C}$  to  $486^{\circ}\text{C}$ . A decreasing trend in solubility is generally observed with increasing alkyl chain length. The variability in solubility data increased due to the difficulty of measurement of solubilities. The primary reason for such a problem is due to emulsion formation during flask shaking, cross-contamination, and insufficient low analytical detection limit. According to Ellington, phthalate esters with long alkyl side chains may rotate and fold into aqueous solutions to resemble a branched-alkyl chain which is lower in energy. The general argument is that the effective molar volume of an unfolded chain is higher than the folded configurations. Branched-chain isomers in general have greater water solubilities than straight-chained isomers. DEHP exhibited a fourfold greater measured solubility than di-n-octyl-phthalate. Although the trend in vapor pressure is not as pronounced as solubilities, vapor pressure declines with an increase in alkyl chains. Di-methyl-phthalate (DMP) has a vapor pressure of around 0.3 Pa which is several orders of magnitude higher than di-tri-decyl-phthalate (DTDP) [76].

Variability exists in vapor pressure measurement as well, with variability increasing with alkyl chain length. Measurement problems below  $10^{-6}$  Pa are unreliable. Extrapolation of the relationship between vapor pressure and molar volume is more reliable than the measure values for vapor pressures less than  $10^{-4}$  Pa [76].

The octanol-water partition coefficient ( $K_{\text{OW}}$ ) is used to predict the partitioning of the substance between water and lipids. So, the octanol-water partition coefficient indicates the equilibrium distribution of a substance between water and octanol.  $K_{\text{OW}}$  is measured by putting the test substance in a two-phase mixture of octanol and water and measuring the resulting

equilibrium concentration in both phases. The major disadvantage of this method is for hydrophobic substance shaking promotes the formation of emulsions thus causing concentration in water to be higher than the solubility in water. With an increasing alkyl chain length  $K_{ow}$  of phthalate esters increases indicating greater hydrophobicity.  $K_{ow}$  of DMP is about ten orders of magnitude lower than DTDP. Solubilities in octanol decrease very gradually (order lower in magnitude) from DMP to DTDP. Although hydrophobicity increases, lipophilicity does not increase with an increase in alkyl chain length but decreases slightly [76]. These structural properties can be the reasons that the phthalates are difficult to be removed using aqueous washing from the PPE.

### 3.2.2 Toxicology of phthalates

Phthalates have low acute toxicity  $LD_{50}$  values of 1-30 g/kg body weight. The short-term and long-term studies indicated adverse effects on the liver, kidneys, thyroid gland tissue, etc. All phthalates were tested negative for mutagenicity and genotoxicity. Dibutyl phthalate (DBP) has indicated tumor-producing activity, DEHP studies in rodents have shown to produce hepatocellular carcinoma along with several other effects. In recent years phthalates have raised concerns over disrupting endocrinal systems, having adverse effects on reproduction and development in humans. Ambient monitoring studies for indoor air demonstrated elevated levels of dibutyl phthalates (DBP) is 600-1200 ng/m<sup>3</sup>, DEHP 150-450 ng/m<sup>3</sup>, DEP >350-600 ng/m<sup>3</sup> ng/m<sup>3</sup> [93]. An interesting study of various phthalates and cohort studies of children in Sweden showed that the presence of benzyl-butyl-phthalate (BBP) in household dust was associated with rhinitis and eczema, while DEHP was associated with asthma even though the study was classified as suboptimal (meaning the dose-response relationship cannot indicate a specific symptom) the associations cannot be undermined. The study concluded with the associations of

the presence of BBP and DEHP with allergies and asthma [77]. The United States Environmental Protection Agency under the Safe Drinking Water Act regulates DEHP levels that are set to a maximum of 6 µg/L [78].

### *3.2.3 Removal of phthalates*

Phthalates are a systematically synthesized class of chemicals that make them highly stable. Hence, phthalates do not degrade easily in the environment. The vast literature available on the removal of phthalates has been focused majorly on the water purification application. Various methods have been studied to remove phthalates that include advanced oxidation processes, coagulation and flocculation, and adsorption. Microbial degradation has been studied extensively for both isolated and mixed cultures in aerobic and anaerobic conditions. A majority of researchers consider microbial degradation as the most practical approach to remove phthalates from the environment [78].

#### *3.2.3.1 Advanced oxidation processes*

The mechanism for advanced oxidation processes (AOP) is to add or produce highly reactive particles that can oxidize phthalates. Several different approaches have been used in the past that combines the oxidation process with other methods such as photochemical degradation of diethyl phthalate (DEP) via UV/H<sub>2</sub>O<sub>2</sub>, DEHP, using Fenton's reagent to degrade along with artificial UV light (photochemical degradation) of DMP, photocatalytic ozonation of DBP, DEHP on TiO<sub>2</sub> film. Ultrasonication combined with the oxidation process has also been used in the degradation of phthalates [79] [80] [81] [82] [83] [84].



### 3.2.3.2 Adsorption of phthalates

#### 3.2.3.2.1 Activated carbon

Activated carbon has been used in the treatment of industrial wastewater. Phthalates have low solubility, high hydrophobicity that makes activated carbon an effective adsorbent. The adsorptive capacity of the activated carbon increased (1.7 times) by modifying with tetrabutylammonium (TBA) and copper [85]. The adsorption studies with activated carbon indicated that adsorption was found to be dependent on the pH of the aqueous solution [86]. Phthalic acid has one hydrophobic group and two carboxylic groups that result in a higher negative charge at pH greater than 3. The study of using activated carbon for the treatment of industrial wastewater was tested for four different pH values and it showed that adsorption decreased by increasing pH values [78]. Various forms of carbon have been used in the research studies such as pine nutshell carbon, carbon from pulverized phoenix leaves that removed phthalates from the aqueous solution [87] [88].

#### 3.2.3.2.2 Cyclodextrin

The  $\beta$ -cyclodextrin forms inclusion complex compounds with phthalate esters during their removal from aqueous solution, thus phthalic acid esters get adsorbed onto  $\beta$ -cyclodextrin or its cross-linked polymer using epichlorohydrin. The NMR spectroscopy showed that cyclodextrin forms hydrophobic cavities that adsorb phthalate esters. The phthalate esters form complex compounds with cyclodextrin that can be measured with fluorescence intensity. The stability complexes were quantified by calculating stability constants. The values of constants increased with an increase in the alkyl chain length of the esters which showed that higher alkyl chain lengths of phthalates esters form stable complexes. The exception to this rule was DEHP since the ethyl groups provided steric hindrance to enter into the cavity. The adsorption

efficiency was different for different phthalates which averaged out to around 63% [89]. Thus, compounds like cyclodextrin can be used in the modification of surfactants to facilitate the removal of phthalates from PPE.

#### 3.2.3.2.3 Biodegradation

Biodegradation is the prominent process in degrading phthalate esters followed by the photolytic oxidation process. Photolytic oxidation generally occurs in the atmosphere while biodegradation happens in all media. Phthalate esters break down into alcohol and monoester. Both aerobic and anaerobic degradation have a similar mechanism. The monoesters are further degraded into phthalic acid by enzymes. The cleavage of ester linkage via hydrolysis is the first step into degrading phthalates. In water and soil, aerobic degradation half-lives increase with increasing alkyl chain [90]. Rates of aerobic degradation in soils were 2 to 5 times slower than that in the aquatic medium. The exception is BBP since it contains two straight alkyl chains and has a different mechanism. Aerobic degradation is faster than anaerobic degradation [91]. In microbial degradation, bacteria are studied extensively as compared to other faculties.

##### 3.2.3.2.3.1 Bacteria

The majority of phthalate degrading bacteria have a rod-like structure. The majority of the bacteria such as *Arthrobacter sp.*, *Pseudomonas sp.*, *Sphingomonas sp.*, *Burkholderia sp.*, and *Acinetobacter sp.* are strictly aerobic [90]. The cultures are isolated and the samples range from soil samples of sewage, river sludge, sediments, etc. Various bacteria degrade specific phthalates such as *Camelimonas sp.* degraded 56% DMP after 72 hours [92], and *Arthrobacter sp.C21* removed 100% DBP after 70 hours [93]. The *Rhodococcus sp.LA* removed phthalates DMP(100%), DEP (100%), and DBP(97.2%) after 6 days of incubation [94]. Some of the strains

are facultative anaerobic (can act in given conditions) such as *Bacillus sp.*, *Serratia sp.*, *Enterobacter sp* [90].

#### 3.2.3.2.3.2 Fungi

Several studies have shown that various fungi can degrade phthalate esters. The mycelial fungi, *Aspergillus parasiticus*, *Fursarium subglutinas*, and *Penicillium funiculosum* can degrade DEHP completely either individually or work in groups [95]. BBP was completely degraded by *Pleurotus ostreatus* within 24 hours [96]. Several other fungi that including *Aspergillus niger*, *Paecilomyces sp.*, *Penicillium sp.*, *Trichoderma sp.*, *Fursarium oxysporum*, *Trichosporon sp.*, have been reported to degrade phthalates [97]. The fungi have extracellular ligninolytic enzymes (lignin peroxidase, manganese peroxidase, laccase) that provide fungi the ability to degrade a variety of chemicals [90].

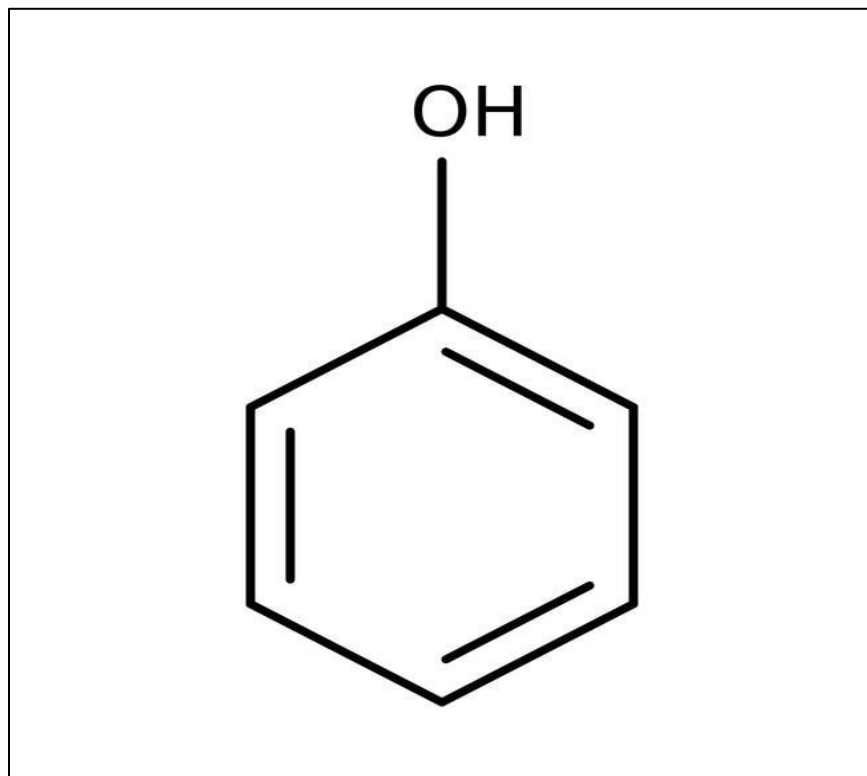
#### 3.2.3.2.3.3 Anaerobic degradation of phthalate esters

Anaerobic microbes such as *Clostridium sp.*, *Bacillus sp.*, *Pelotomaculum sp.*, *Pseudomonas sp.*, have been studied as the bacteria that degrade phthalate esters. The methanogenic (methane generating) consortia degrade phthalates in the complex anaerobic environment [90]. The river sediments of Taiwan indicated methanogenic, sulfate-reducing bacteria, eubacteria degraded phthalate esters [98]. The anaerobic degradation rates of short-chain compounds are higher than long-chain compounds [90]. The half-lives of DEHP: 25.70 days, DEP:15.40, DBP:9.40 days have been reported in anaerobic conditions [98]. The mesophilic anaerobic conditions rapidly degrade phthalate esters [99].

### 3.3 Phenols

Phenols are cyclic compounds containing a hydroxyl group attached to an aromatic ring (Figure 3-3). Most phenol derivatives are found in soils, plants, and the natural decay of

lignocellulosic materials. Phenols are a pollutant that is found largely in industrial effluents, oil refineries, pulp and paper manufacturing industries, pharmaceutical industries, plastic and varnish industries [101].



*Figure 3-3: Structure of phenol.*

### *3.3.1 Physical and chemical properties*

Hydroxyl groups attached to aromatic rings provide sites for hydrogen bonding, which makes phenols soluble in water. Also, cleaving of the benzene ring is difficult which provides stability in nature. The valence electrons of the carbon atoms in phenolic structures can delocalize and form resonant structures. The presence of electron-withdrawing and electron-donating groups on phenolic rings shift valence electrons which can be understood by resonance. The phenolic derivatives are formed by substituting at positions relative to the initial hydroxyl group and are named accordingly such as o-cresol (ortho-cresol), p-nitrophenol (para-

nitrophenol), etc. Phenolic compounds form phenoxide ions when dissolved in water and are slightly acidic compared to regular alcohols [100].

Phenols are soluble in most organic solvents and slightly soluble in water at room temperature. Phenols become completely soluble in water starting at 68°C. Phenoxide ion is more stable since the negative charge is delocalized on the benzene ring. The pH of phenolic water is around 5-6. There are 3 important categories of phenols: pyrogallols, chlorophenols, and nitrophenols. The  $K_{OW}$  value for phenol is 1.46, indicating solubility in water. The benzene ring is non-polar thus limiting the solubility in water but at a temperature above 68°C, it is completely soluble in water [101]. Two aromatic six-carbon rings, each with or without substituents can form biphenols by covalent bonding. Although phenolics are sparing to moderately soluble in water, the aqueous solubility and acidity are influenced by the type of substituents and the position of the substituents. The effects are significant if the electron-withdrawing groups are located at ortho and para positions. The  $pK_a$  for phenol is 10 and for p-nitrophenol is 7.2 [100].

### 3.3.2 Toxicity of phenols

The toxicity of phenols varies and is often expressed in ranges of values. This indicates the fact that the toxicity of phenols has no single value since it is a function of biological response to the chemical. Hence, toxicity depends on various factors such as the nature of the chemical, duration of exposure to the chemical, mode of exposure, test conditions, etc. Phenols have teratogenic, carcinogenic and mutagenic effects [102]. When generalized, toxicity decreases in the order: Phenol > p-cresol > o-cresol > m-cresol > catechol

These phenols do not bioaccumulate to a large extent; and, when diluted, biodegradation occurs rapidly into non-toxic products. Half-lives of phenols can range from days to weeks. The toxicity of phenolic molecules increases with the bulk of the molecule that includes branching,

substitutions. Strong electronegative groups increase the toxicity of phenols such as halogens. Halogenated phenols are more toxic, less biodegradable and their toxicity increases with the degree of halogenation such as pentachlorophenol [100]. The IDLH limit of pentachlorophenol according to NIOSH is (250 ppm)  $960 \text{ mg/m}^3$  for airborne exposure. Phenols in higher concentrations cause protein degradation, tissue erosion, irritation to the skin. For an 8-hour shift OSHA set TWA at 5 ppm, NIOSH suggested a PEL of  $20 \text{ mg/m}^3$  for a 10-hour per day work shift [103].

### *3.3.3 Application of phenols*

Pentachlorophenol (PCP) is mainly used as a wood preservative. Brominated phenols since the 1970s are used as flame retardants. Bisphenol A is used in polycarbonates and resins that have been widely used in the food packaging and electronics industry. Chlorinated phenols have been used in the dyes, pigments, and resins, as a raw material in manufacturing ingredients for pesticides. Alkylphenols have been used in gasoline additives, dyes, polymer additives, surfactants, herbicides, and lubricant oil additives. Phenol derivatives are used in laser and inkjet printing. Phenolics and epoxy coatings are used in pipes to prevent corrosion. Phenol is one of the oldest disinfectants in hospitals. It has also been used in mouthwash, ointments, etc [102].

### *3.3.4 Removal of Phenols*

Phenols in industrial effluent have toxic effects and are difficult to biodegrade. The research on various removal techniques of phenols has gained considerable attention in the last 2 decades. A variety of treatments such as adsorption, incineration, chemical oxidation, and wet oxidation have been used to remove phenols from aqueous solutions [102].

#### *3.3.4.1 Chemical oxidation*

The main chemical oxidizing agents that are used are chlorine, ozone which convert phenols into hydroquinone and then form a quinone. Further oxidation can destroy the aromatic rings eventually resulting in carbon dioxide and water. If a stoichiometric amount of chlorine (42 parts of chlorine per part of phenol) is added at pH 7.7 phenols can be completely decomposed. Water treatment plants used this process to achieve super-chlorination. Ozonation is another technique that is effective but very costly. For ozonation, approximately 5.8 parts of ozone per part of phenols are required to achieve complete oxidation [102].

#### *3.3.4.2 Carbon adsorption*

In many wastewater-treatment plants, activated carbon is used to decontaminate water. Activated carbon in powdered form can absorb around 25 gm of phenols/ 1000 gm of activated carbon along with other compounds from potable water. This process is economical and effective. At low pH levels, phenols get adsorbed more effectively since phenols form salt at alkaline pH [102].

#### *3.3.4.3 Solvent Extractions*

In solvent extractions two immiscible or partially soluble liquids, such as iso-kerosene, benzene, light tar oil, or phenosolvan, are brought into contact to transfer one or more components while extracting phenol. Phenosolvan has a higher partition coefficient than benzene hence it is more effective in extracting phenol. The extracted phenol can be washed out by adding sodium hydroxide which results in the formation of salts and benzene can be recycled. Light catalytic cracking oils are used as extractors in the petroleum industry and coke oven oils are used as extractors in the coking industry. Solvent choice and system design play a vital role

in determining process efficiency. The disadvantage of this method is that it's uneconomical and requires a high flow rate of solvents to remove phenols [102].

#### *3.3.4.4 Biodegradation*

The biodegradation of organic waste from water has gained attention in the last decade. Many researchers consider it a promising alternative and economical method. It costs 5 to 20 times less than many chemical degradation methods [101]. A variety of microorganisms such as enzymes, bacteria, and fungi can degrade phenols. Bacteria and fungi have been studied extensively over the years [102]. The biodegradation depends on biotic as well as abiotic factors. The chemical structure is the main parameter which varies with the number and position of the substituents, degree of branching, etc. Generally, ortho and para-substituted phenols are more degradable than meta. A higher number of substitutions make compounds more toxic and less biodegradable [104].

##### *3.3.4.4.1 Enzymatic oxidations*

Peroxidases catalyze the oxidation of organic and inorganic compounds. Such enzymes increase the rate of reactions where they form phenoxy radical which is highly reactive and forms an insoluble film that can be filtered out. Several microorganisms need organic contaminants mainly carbon as a source of energy to carry out their metabolic activities. Biodegradation of an organic pollutant also depends on several other factors such as pH, temperature, availability of oxygen. Generally, microorganisms convert all the contaminants to harmless compounds such as water and CO<sub>2</sub>. Bioremediation can be classified as in situ or ex-situ. The in-situ approach is less expensive as compared to ex-situ although the latter one is more effective since it is controlled and more predictable [102].



#### 3.3.4.4.2 *Bacteria*

Many lab-scale studies were able to isolate and characterize bacteria to test the efficiency of degrading bacteria [101] [105] [106] [107] [108] [109]. Bacteria from the *Pseudomonas* genus have been used commonly to biodegrade phenols. *Pseudomonas putida* has demonstrated high removal efficiency of phenols and can operate in extreme environments [101]. A consortium of 22 pure cultures, dominated by *Acinetobacter* sp. and *Bacillus* sp. was able to degrade phenols in a lab-scale experiment after incubation of 104 days. The consortium also reduced the chemical oxidation demand of the wastewater [106].

#### 3.3.4.4.3 *Fungi*

Fungi play a significant role in degrading toxic chemicals in the biosphere and are capable of consuming carbon sources by metabolizing them through enzymatic mechanisms. Yeasts such as *Candida tropicalis* and *Fusarium flociferum* metabolize phenols by using carbon as the energy source. Strains of *Penicillium*, *Aspergillus*, and *Graphium*, *phanerochaete*, disintegrate aromatic compounds. The white-rot fungi, *Trichoderma harzianum* can degrade chlorophenols [101] [104].

The above literature highlighted the differences in chemicals and physical properties of different classes of compounds. The removal of these compounds has been studied extensively in the bioremediation domain. Some of the common techniques that have been used for all three classes of compounds include: Chemical degradation that includes oxidation, sorption, and biodegradation that includes incorporating microbes. Although oxidation is a quicker process of all the NFPA 1851 standard prohibits from using the oxidation process to protect the outer shell [14]. The structure-property relationship has a significant role in the removal of these contaminants. Some of the important points to consider: (1) Phenols are more polar as compared

to PAHs and phthalates. This shows more susceptibility for aqueous removal of phenols as compared to the other two. (2) PAHs and phthalates are non-polar and more hydrophobic that indicating low aqueous mobility. This clearly explains the low removal efficiency of these contaminants in the laundering process. (3) Phthalates are engineered structures hence have high stability. Their long alkyl chain lengths provide exceptional stability thus making them sparingly lipophilic. Their affinity towards organic matter makes them deposit in sediments. From various contamination studies, it was clear that the smoke particles are the ideal surfaces that provide a high surface area for these contaminants to get adsorbed due to their low particle size. This particulate matter lodged in the interstices of fabric material, in the non-woven batting is difficult to remove due to constraints in the washing procedure. To remove these contaminants from a soiled PPE, it is important to provide compounds with higher surface area in an aqueous solution that have a higher affinity for these compounds which will improve the desorption process. Hence, biodegradation and adsorption using organic matter are potential routes in efficiently removing these compounds.

## Chapter 4: Surfactants

The previous sections highlighted the low removal of fireground contaminants for the firefighters' PPE during the laundering process. The washing of the PPE is performed according to the NFPA 1851 standard prescribed guidelines as discussed in Chapter 2. Thus, the removal of contaminants majorly depends on the properties of the surfactants. The surfactants that are used for washing PPE are designed in compliance with the NFPA 1851 standard that certainly affects the properties of a surfactant and its interaction with the fabric and contaminants. In chapter 3 we studied different physical and chemical properties of PAHs, phenols, and phthalates and their removal. This guided us in investigating the surface activities of the aqueous solution and improving it. Thus, it is important to consider the activity of the surfactants and what parameters affect it in an aqueous solution.

The Surfactants are surface-active agents that are generally divided into two parts, a hydrophilic portion and a hydrophobic portion. The hydrophilic portion can be cationic, anionic, zwitterionic (both charges are present), or nonionic and interacts with polar solvents like water through dipole-dipole or ion-dipole interactions. The hydrophobic chain generally consists of carbon chains that weakly interact with water. The amount of free energy per unit area is called as interfacial energy which is the work done to expand the interface. The nature of the two phases that are involved, and the structure of surfactants are driving factors for the interaction of surfactants. Two important phenomena that need to be considered when studying surfactants are [110]:

1. Effects of surfactants on stabilization of various dispersions and emulsions.

2. Orientation of surfactant ions or molecules that affects the adsorption of surfactants on various interphases. Accurate measurements of the adsorption and orientation of molecules are required.

#### 4.1 Anionic Surfactants

These surfactants have a negative charge on the head (anionic) hence it's an anionic surfactant Figure 4-1 They are the oldest and most widely used surfactants in the industry due to their low cost. Anionic surfactants represent approximately 70% of the total consumption of surfactants. The polar head group is at the end of the chain and usually, a linear hydrophobic chain is preferred due to their effectivity and easy degradability as compared to branched chains. The number of carbons in the chains ranges from 8 to 16.

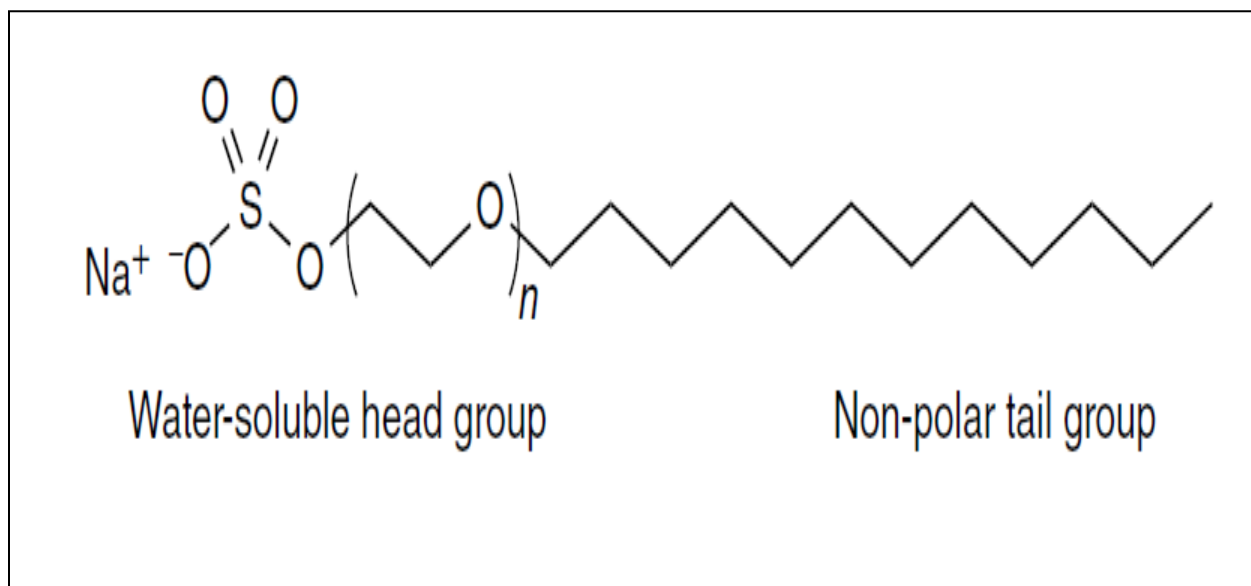


Figure 4-1: Anionic surfactant.[111]

The counterion  $\text{X}^+$  for anionic surfactants is generally a sodium ion. Commonly used hydrophilic groups in anionic surfactants are: carboxylates ( $\text{C}_n\text{H}_{2n+1}\text{COO}^-\text{X}^+$ ), sulfates ( $\text{C}_n\text{H}_{2n+1}\text{OSO}_3^-\text{X}^+$ ), sulfonates ( $\text{C}_n\text{H}_{2n+1}\text{SO}_3^-\text{X}^+$ ), phosphates ( $\text{C}_n\text{H}_{2n+1}\text{OPO}(\text{OH})\text{O}^-\text{X}^+$ ). Carboxylates were found in the earliest soaps such as sodium stearate ( $\text{C}_{17}\text{H}_{35}\text{COO}^-\text{Na}^+$ ) and

sodium myristate ( $C_{14}H_{29}COO^-Na^+$ ). The alkyl groups in the chains contain unsaturated compounds like sodium oleate. Most of the soaps are prepared from the saponification of triglycerides of oils and fats. Low toxicity, cost, and biodegradability are the main advantages of these soaps. Major limitations include that they are ineffective with hard water where bivalent ions such as  $Ca^{+2}$  and  $Mg^{+2}$  are present resulting in higher precipitation of soaps. Adding ethoxylated groups with the general structure  $RO(CH_2CH_2O)_nCH_2COO^-$  to ester carboxylates containing multiple COOH groups helps in decreasing precipitation, increasing water solubility, and preventing hydrolysis as they become chemically stable. Such modified ether carboxylates are more compatible with electrolytes, have good compatibility with amphoteric, nonionic, and cationic surfactants. Sarcosinates containing amide groups having general structure  $RCON(R')COO^-$  are compatible with anionic, cationic, non-ionic, and have good solubility in alkaline media but limited in acidic and neutral medium. The ester carboxylates are highly soluble in water but have a limitation of hydrolysis [110] [111] [112].

Sulfates are the largest class of synthetic surfactants produced from reacting sulfuric acid with alcohol. Alcohols are generally sulfated using chlorosulfonic acid or  $SO_2$ /air mixtures. Such reactions produce highly unstable compounds that hydrolyze the alcohol in an acidic medium. Hence, sulfonates are preferred. The alkyl chain length and sulfate group determine the properties of sulfate surfactants. Sodium dodecyl sulfate is also known as sodium lauryl sulfate is the most common surfactant from this category. Salts of alkali sulfates have good solubility in water and are fairly stable at room temperature. However, below room temperature, these surfactants turn into a soft paste decreasing the solubility [110] [111] [112].

The alkyl sulfates give good foaming properties with an optimum carbon chain length of 12-14 carbon atoms. Sulfate surfactants are modified to change their properties, the most

common modification includes adding ethylene oxide (EO) in the chain that produces alcohol ether sulfates. This improves the solubility and compatibility with the electrolytes present in the medium. In sulfonates, sulfur is directly attached to a carbon which increases chemical stability against hydrolysis. Alkyl-aryl sulfonates are the common type of surfactants in this family which are prepared by reacting sulfuric acid with alkyl aryl hydrocarbons. Naphthalene, alkyl naphthalene sulfonates are used as dispersants. Nonlinear paraffins are reacted with sulfur dioxide and oxygen to prepare paraffin sulfonates. These surfactants have excellent water solubility and biodegradability [110] [111] [112].

Linear alkylbenzene sulfonates are manufactured from alkylbenzene. Their properties are influenced by chain length. The linear alkylbenzene sulfonates are manufactured from an alkyl chain length with 8 to 15 carbon atoms and alkylbenzene. The primary disadvantage of this class of surfactant is that it has a harsh effect on skin surfaces which inhibit their use in cosmetic and personal applications [110] [111] [112].

The  $\alpha$ -olefin sulfonates are prepared by reacting  $\alpha$ -olefin with sulfur trioxides having alkyl chain lengths between 12-16 carbon atoms and 16-18 carbon atoms. Phosphate containing anionic surfactants are prepared by adding alkyl phosphates, alkyl ether phosphates with fatty alcohol or alcohol ethoxylates with phosphorous pentoxide ( $P_4O_{10}$ ) as a phosphorylating agent. The product is a mixture of mono and diesters of phosphoric acid. This mixture affects the physio-chemical properties. This class has properties intermediate between non-ionic and the sulfated derivatives. They have anti-corrosive properties hence are used widely in the metal industry. Other groups include isethionates, phosphate-containing anionic surfactants, taurates [110] [111] [112].

## 4.2 Non-ionic surfactants

Non-ionic surfactants are the second largest class of surfactants. They have either a polyether or polyhydroxy unit as the polar head Figure 4-2.

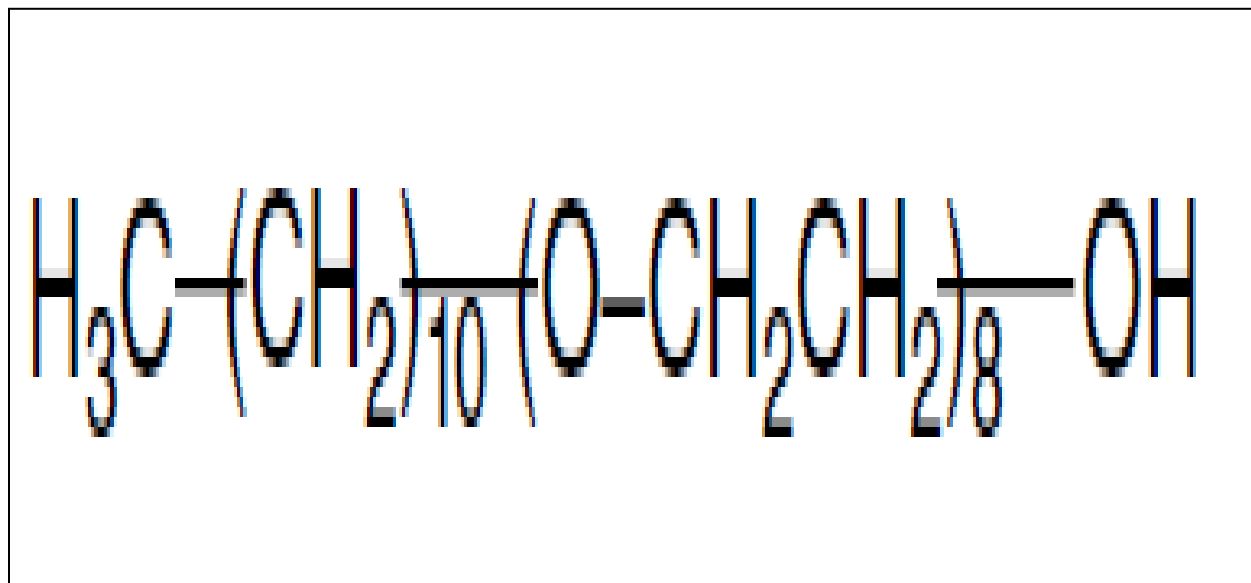


Figure 4-2: Nonionic surfactant.[111]

Polyether-based surfactants dominate the market and are prepared by the polymerization of ethylene oxide. The polar chain consists of 5-10 ethylene oxide units. For dispersant application, longer chains are required. Ethoxylation is carried out in alkaline conditions with any active hydrogen-containing material such as fatty alcohols, fatty acids, fatty amines, alkylphenols [110] [111] [112].

Sorbitan esters, alkyl glucosides, polyglycerol esters, sucrose esters are examples of polyhydroxy-based surfactants. The sorbitan is obtained by dehydrating sorbitol. The fatty acid esters of sorbitan are commercially available as Span<sup>®</sup> and the ethoxylated products are commercially available as Tween<sup>®</sup>. The sorbitan esters are mainly used in the food and drug industry. The sorbitan esters are soluble in organic solvents [110] [111] [112].

Polyoxyethylene-based surfactants can also be customized with high precision with regard to the average number of oxyethylene units added to the specific hydrophobe such as fatty alcohol. Alkylphenol ethoxylates are prepared by reaction of ethylene oxide with alkyl phenol mostly nonylphenol. Such surfactants are economical, dispersion and emulsification properties but are toxic to the aquatic environment. Amine ethoxylates are prepared by ethylene oxidation of primary and secondary amines. At low pH and a low number of ethylene oxide units, amine ethoxylates function like cationic surfactants. To function like a nonionic surfactant, it requires neutral pH and high ethylene oxide units. The physicochemical properties of ethoxylates depend on the temperature. At higher temperatures, they become more hydrophobic [110] [111] [112].

#### 4.3 *Cationic Surfactants*

Cationic surfactants are surfactants with a positive ion ( $X^+$ ) for the head. This class of surfactant ranks third in consumption. The vast majority of cationic surfactants are nitrogen-based. Amines and quaternary ammonium-based products are widely used (Figure 4-3). The amines have to be in a protonated state to function as cationic; therefore, they cannot be used at higher pH. Quaternary ammonium compounds with the formula  $R^1R^2R^3N^+X^-$  where R represents an alkyl group and  $X^-$  is chloride ions are prepared by reacting an appropriate tertiary amine with an organic halide or organic sulfate. These compounds are not pH sensitive. The alkyl trimethyl ammonium chloride is a commonly used cationic surfactant which contains 8-18 carbon atoms [110] [111] [112].



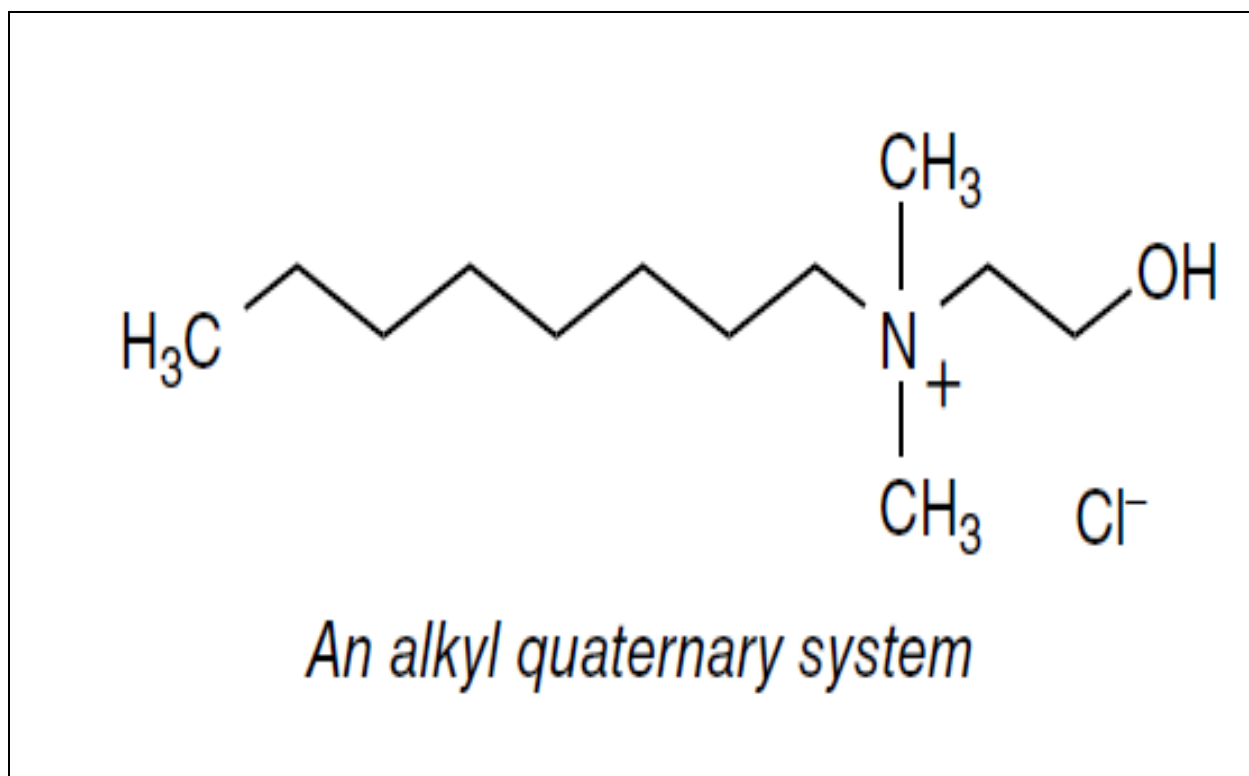


Figure 4-3: Cationic surfactant. [111]

Dialkyl dimethyl ammonium chloride is another class of surfactant that is used commonly but is less soluble than the previous one. These surfactants with two alkyl chains are used as fabric softeners [110] [111] [112].

Phosphonium, sulfonium, and sulfoxonium surfactants are also used as cationic surfactants although their industrial usage is very low due to the higher cost of production. Cationic surfactants are more soluble with a single alkyl chain since two or more long alkyl chain length makes them dispersible in water and more soluble in organic solvents. These surfactants are compatible with non-ionic surfactants, inorganic ions, and hard water but incompatible with metasilicates, highly condensed phosphates, protein-like materials, and anionic surfactants [110] [111] [112].

Cationic surfactants are stable over the changes in pH, tolerate electrolytes, and are insoluble in hydrocarbon oils. Cationic surfactants that are hydrolytically stable have higher

aquatic toxicity. Most of the metal surfaces, plastics, membrane surfaces are negatively charged; hence cationic surfactants are used primarily since they get adsorb at these surfaces [110] [111] [112].

#### 4.4 Amphoteric surfactants

This class of surfactants contains both cationic and anionic groups. The derivatives of trimethylglycine  $(\text{CH}_3)_3\text{NCH}_2\text{COOH}$  (betaine) are the most common surfactants in this class. Betaine (Figure 4-4) was discovered by *Schiebler* by isolating sugar-beet juice. These alkyl chain derivatives are called alkyl dimethyl glycinate.

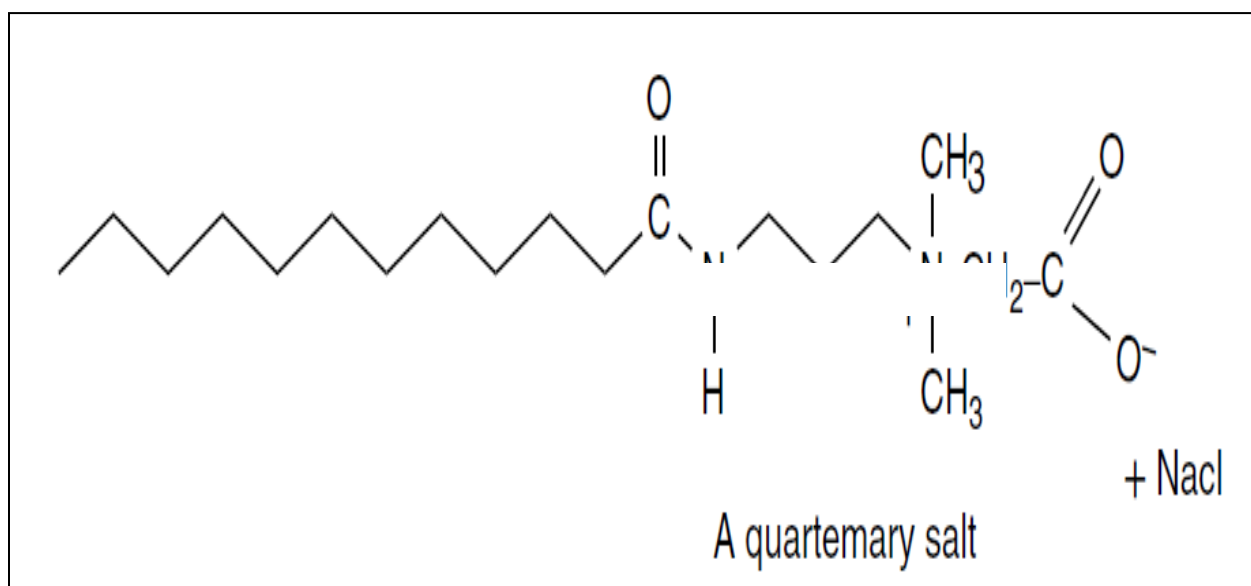


Figure 4-4: Betaine structure.[111]

Imidazoline derivatives Figure 4-5, N-alkyl amino propionates are another major class of surfactants in this category. The distinctive feature of the amphoteric surfactant is its dependence on the pH of the solution it is dissolved in. For acidic solution, it functions like a cationic surfactant as the molecule acquires a positive charge and for alkaline pH, it functions like an anionic surfactant due to negative charge acquisition. The sulfate-containing surfactants and the sulfonates remain amphoteric even at very low levels of pH. The imidazoline surfactants are

synthesized by reacting aminoethylethanolamine with fatty acids and then treating the product with chloroacetate [110] [111] [112].

Amphoteric surfactants also known as zwitterionic are soluble in water. The solubility is minimum at the isoelectric point and these surfactants demonstrate excellent compatibility with other surfactants. The surface activity of amphoteric surfactants depends on the distance between the charged ions and is maximum at the isoelectric point. The pH affects the charge present on the surfactants which affects the properties like wetting, detergency, and foaming. The zwitterionics have zero net charges hence they are compatible with high electrolyte formulations. Amphoteric surfactants demonstrate excellent dermatological properties and hence are used in cosmetic products [110] [111] [112].

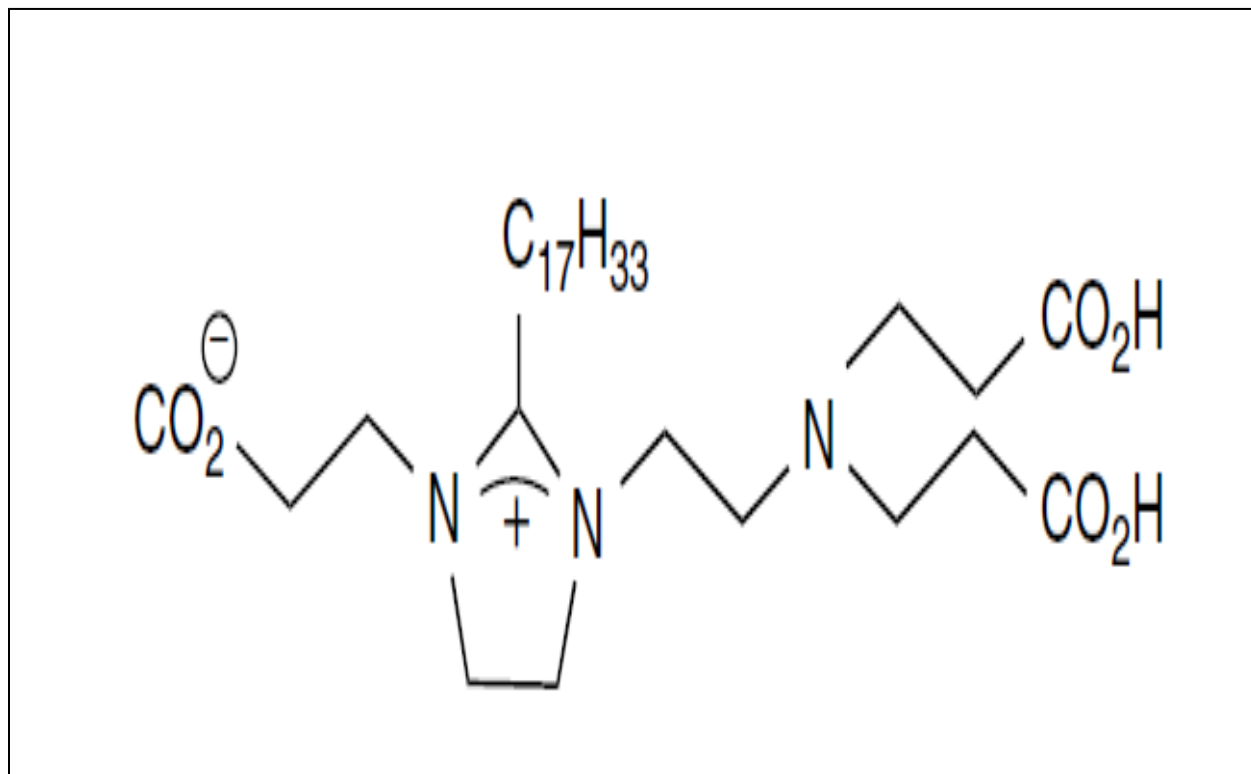


Figure 4-5: Imidazoline structure.[85]

## 4.5 Wetting

The concept of wetting is very important from the application perspective when studying surfactants. Wetting is an interfacial phenomenon in which one fluid phase is displaced partially or completely by another fluid phase from the surface of the solid or liquid. In all the applications, equilibrium aspects need to be considered, and studying interfacial thermodynamics helps in achieving the fundamentals of the same. The contact angle is the parameter that describes wetting.

When a drop is placed on a solid surface, it either spreads completely (complete wetting) or remains as a drop (partial/incomplete wetting) as represented in Figure 4-6

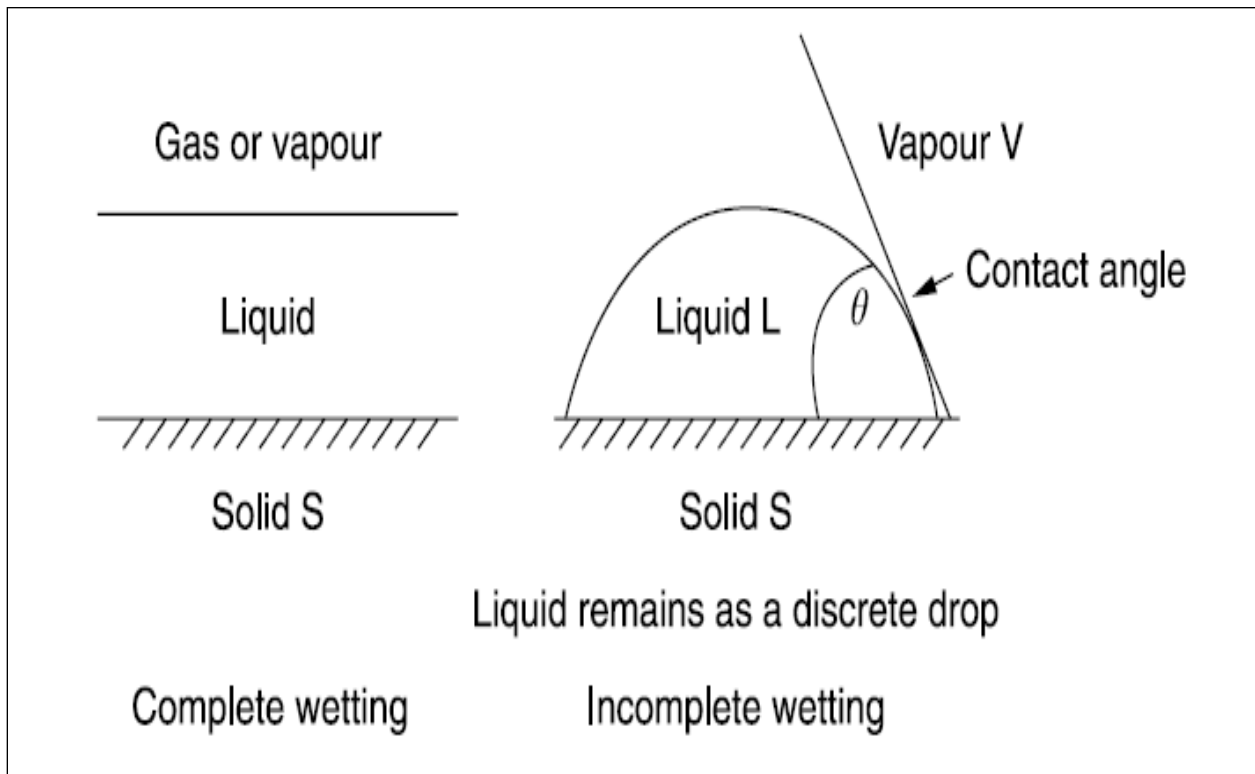


Figure 4-6: Schematic of complete and partial wetting. [110]

The contact angle  $\theta$  is the angle formed between tangent surfaces to solid and liquid surfaces. The wetting line is a wetting perimeter that is referred to as a three-phase line (solid/liquid/vapor). The wetting line is useful in measuring the dynamic contact angle. When a

liquid is dropped on the surface, it takes the shape where the surface energy is minimized for the system. Figure 4-7 represents a system where a liquid drop (L) is placed on a solid surface (S) and in equilibrium with the vapor phase (V).

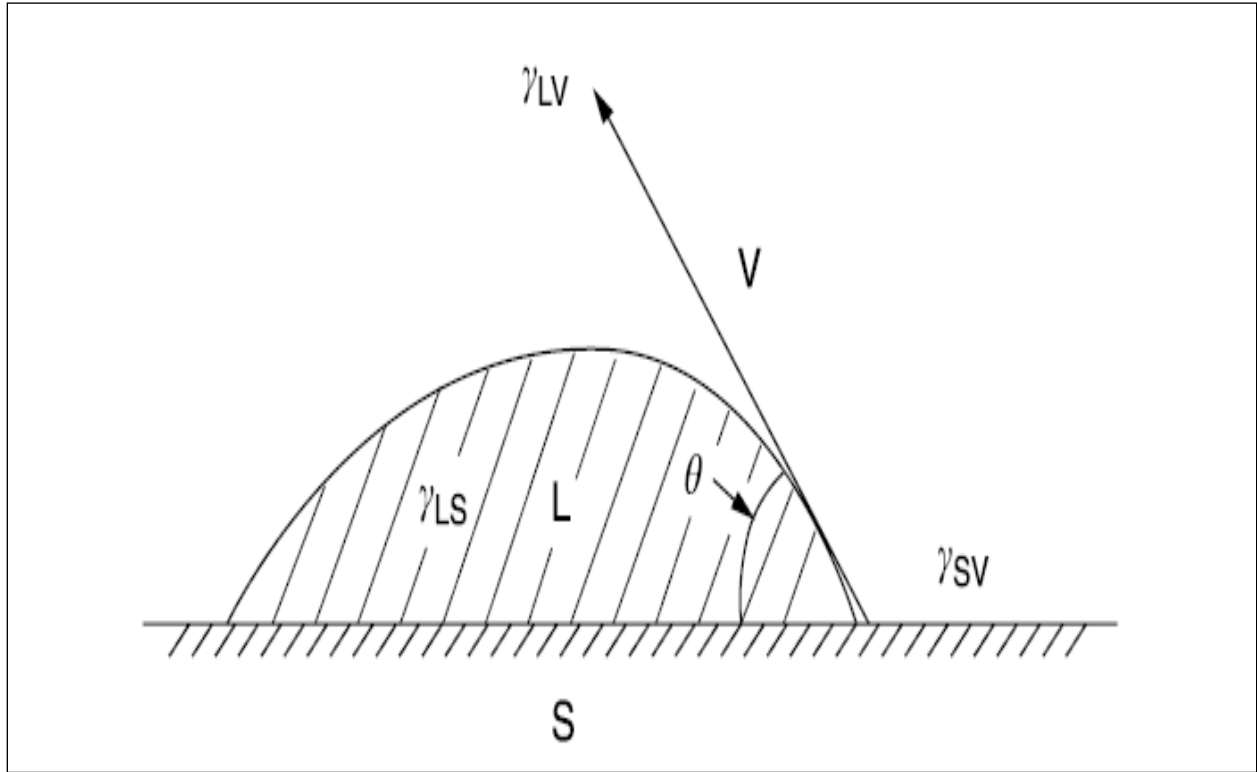


Figure 4-7: Schematic of the balance of surface tensions.[113]

The surface tension ( $\gamma_{SV}$ ) is the surface tension for a solid-vapor boundary,  $\gamma_{LS}$  represents the surface tension for a liquid-solid boundary,  $\gamma_{LV}$  represents liquid-vapor boundary and  $\theta$  is the contact angle at equilibrium. The sum of the forces should be minimum at equilibrium which leads to Young's equation

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta \quad \text{Equation 4-1: Young's equation}$$

Thus, the angle  $\theta$  formed is the balance between the cohesion and adhesion forces on the boundary. For zero interaction between solid and liquid, the equation will be for  $\theta = 180^\circ$

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV}$$

*Equation 4-2: Zero interaction*

and for strong interaction between solid and liquid surfaces:  $\theta = 0$ :

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV}$$

*Equation 4-3: Strong interaction*

Thus, wetting is an important interfacial phenomenon that is applied in various fields from cosmetics, detergent formulations, pharmaceuticals, etc. Wetting agents must have the following properties to be effective: (1) A strong driving force to go to the solid-liquid interface; (2) effectively reduce the surface tension; (3) have a sufficient non-micelle bound surfactant; and (4) borderline water solubility and high critical micelle concentration. All of these properties are demonstrated by a branched, non-ionic surfactant or anionic surfactant hence they are used in commercial formulations [112].

#### **4.6 Adsorption**

Adsorption is the accumulation of concentration at a surface due to intermolecular forces of attraction [114]. The substance that gets adsorbed is called an adsorbate and the surface is called an adsorbent. Surfactants are used in many formulations and provide robust stabilization at high temperatures and pressure. Thus, adsorption plays a very important role in understanding the functioning of surfactants. Adsorption can be understood by describing several interaction parameters that involve various forces such as electrostatic forces, hydrogen bonding, etc [110].

##### *4.6.1 Adsorption of ionic surfactants on hydrophobic surfaces*

This phenomenon depends on the hydrophobic interaction between the alkyl chain of the surfactant and hydrophobic surface and electrostatic interaction plays a relatively smaller role.

The hydrophobic effect is observed when the hydrophobic hydrocarbon parts of the surfactant come in contact thus getting adsorbed on the hydrophobic surface Figure 4-8(a). When the polar surface is present with a low concentration of surfactants, the polar part of the surfactants comes in contact with the surface and gets adsorbed due to the interaction between the surface and the head of the surfactant Figure 4-8(b)). At higher concentrations depending on the strength of the interaction between the surfactant and surface, different scenarios are possible. If the interaction is higher, then a monolayer will be formed that will have all the heads adsorbed on the surface and hydrophobic hydrocarbon tails will be in contact with the solution. This will ultimately result in a second layer formation where all the hydrophobic tails will be attracted to all the other hydrophobic tails which creates a hydrophobic effect. At moderate interaction, micelles or other surfactant aggregation will be formed at the surface. This is due to the hydrophobic interaction will be stronger than the surface and the surfactant head interaction [110] [112]. However, if the same charge is present on the surfactant head and the surface then electrostatic repulsion occurs which will oppose adsorption. Also, if opposite charges are present adsorption is enhanced. The amount of the surfactant adsorbed increases directly with alkyl chain length and the adsorption depends on the magnitude of hydrophobic binding free energy.

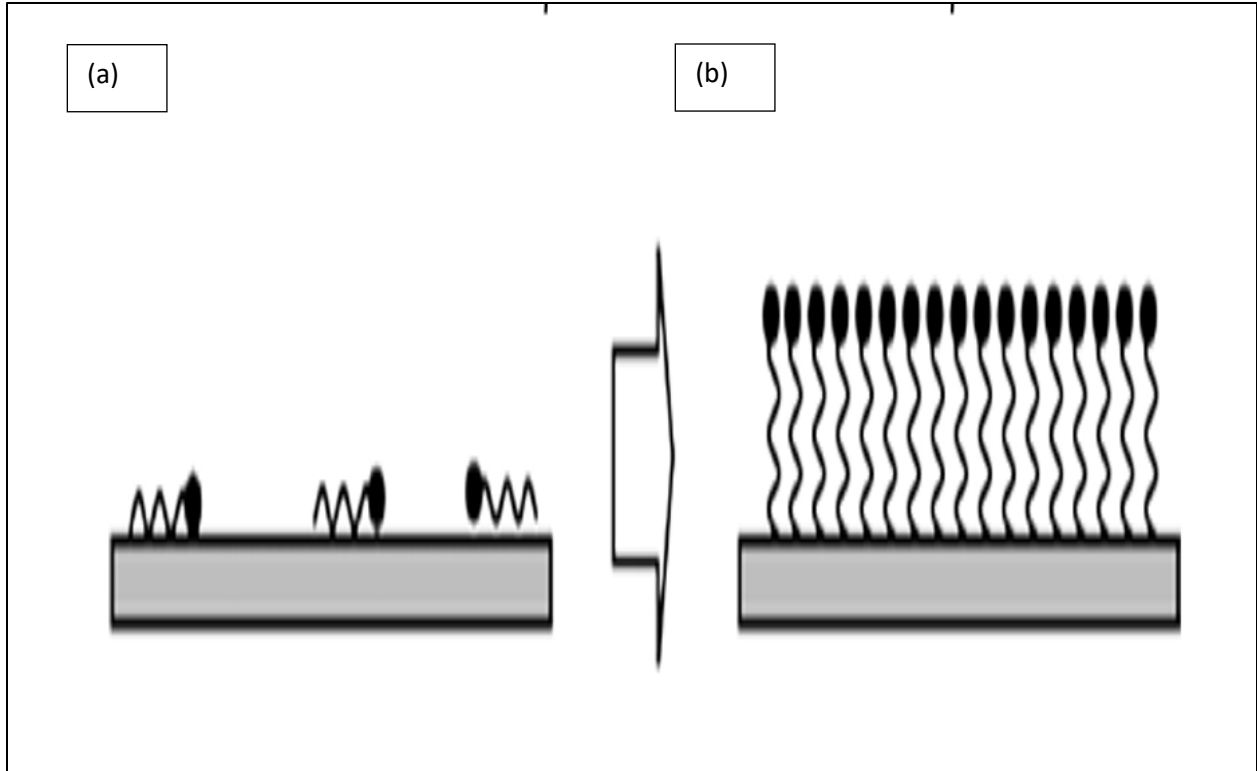


Figure 4-8:(a) At low concentrations surfactants lie down at the surface. (b)at higher concentration monolayer is formed.[112]

Stern-Langmuir isotherm is used to represent the adsorption of the surfactants on the hydrophobic surfaces. When a substrate has  $N_s$  sites ( $\text{mol m}^{-2}$ ) on which  $\Gamma$  moles  $\text{m}^{-2}$  surfactants ions are adsorbed. The surface coverage  $\theta$  is  $\Gamma/N_s$ . Thus, the uncovered surface is  $(1 - \theta)$ . Thus, the rate of adsorption can be expressed using a mole fraction of the surfactant and free surface:

$$\text{Rate of adsorption} = k_1 (C)(1 - \theta) \quad \text{Equation 4-4: Rate of adsorption}$$

where  $k_1 = k_{\text{ads}}$  is the rate constant for adsorption.

$$\text{Rate of desorption} = k_2(\theta) \quad \text{Equation 4-5: Rate of desorption}$$

At equilibrium both the rates are the same hence, we get the equation



$$\frac{\theta}{1 - \theta} = KC$$

*Equation 4-6: Langmuir Equation*

where  $K = k_{ads}/k_{des}$  is an equilibrium constant, describes the partitioning of the surfactant between the surface phase and the solution phase.

The equilibrium constant  $K$  can be related to Gibb's free energy of adsorption using equations

$$(-\Delta G^{\circ}ads) = RT \ln K$$

*Equation 4-7: Gibb's free energy*

Substituting the value of  $K$  in Equation 4-6

$$\theta/(1 - \theta) = C_{ex} p \left[ \left( \frac{-\Delta G^{\circ}ads}{RT} \right) \right]$$

*Equation 4-8: Adsorption isotherm*

Adsorption isotherms theories cannot be used as the only tool in determining the adsorption of the surfactants since it involves multiple parameters. It can be applied only when  $\theta$  is less than 0.1. At higher surface coverage, lateral interaction between the chains is taken into consideration. As the concentration approaches CMC, adsorption may appear as Langmuirian which implies complicated orientation such as electrostatic interaction, counterion binding, horizontal and vertical rearrangement are not considered in adsorption isotherms and may get neglected. Thus, combining adsorption isotherm with other spectrometric methods to understand the overall scenarios for the adsorption [110] [112].

#### 4.6.2 Adsorption of ionic surfactants on polar surfaces

The polar surfaces may contain ionizable groups which lead to additional interaction between the head group and substrate, chain-chain interaction that facilitates the adsorption of

surfactants. Consider the adsorption of surfactant sodium dodecyl sulfonate (SDS) on alumina at pH 7.2 as shown in Figure 4-9. The saturation adsorption  $\Gamma_1$  curve is plotted against equilibrium concentration  $C_1$  on a logarithmic scale. The second curve represents zeta potential  $\zeta$ . Both curves are divided into three different regions (I, II, III).

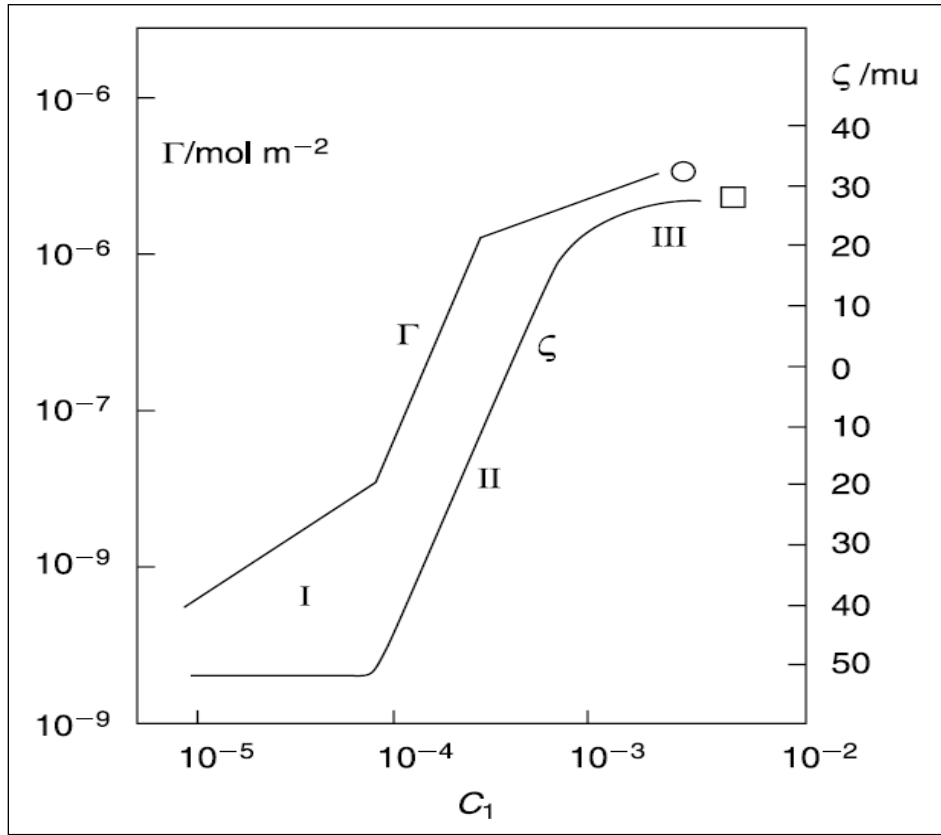


Figure 4-9: Adsorption isotherm of SDS on alumina.[110]

The solution also contains electrolytes that contain  $\text{Cl}^-$  as a counterion. At low concentrations, the surfactants get adsorbed by the ion-exchange mechanism with the counterions that are close to the surface. Thus, the zeta potential is virtually constant and there is a gradual increase in the surfactant adsorption as shown in region I. For region II at critical surfactant concentration, the desorption rate increases with an increase in surfactant concentration. The zeta potential decreases and achieves charge neutralization. After this zeta potential achieves a negative value. This negative zeta potential increases with an increase in the

surfactant concentration. The surfactants aggregate at a much lower concentration than CMC and the concentration in bulk induces micellization at the surfaces. The shapes of these micelles are debatable (Spherical or semi-spherical termed as “hemi-micelles”). Gaudin and Fuerstenau postulated hemi-micelle formations increased the zeta potential in the region II. In other words, critical surfactant concentration can be called critical aggregation concentration. In the hemi-micellization process, at a specific surfactant concentration, once the iso-electric point is exceeded the electrostatic repulsion hinders the process of adsorption decreasing the slope of adsorption isotherm (region III) [110] [112].

#### 4.6.3 Adsorption of nonionic surfactants

The adsorption isotherms for nonionic surfactants in the majority of the cases follow Langmuir adsorption. Although there are several types of nonionic surfactants depending on the polar nature, most of the literature is based on the ethoxylate type. The ethoxylated surfactants are characterized by a large head group compared to the alkyl chain. They are denoted by  $C_x\phi E_n$  where  $x$  is the number of carbons in the chain,  $\phi$  represents  $C_6H_4$ ,  $n$  denoted ethoxylated groups. Various interactions such as adsorbate-adsorbate, adsorbate-solvent, adsorbate-adsorbent can be used to explain various stages of adsorption isotherms as shown in Figure 4-10 aided with the schematics in Figure 4-11. In the first stage (I) Van der Waals interaction is the driving force in adsorption and all other interactions such as surfactant-surfactant interaction are negligible which indicates low coverage. If the surface is hydrophobic then the hydrophobic portion dominates the interaction and for the hydrophilic surface, the ethoxylate groups dominate the interactions. The region II in the isotherm indicates the monolayer saturation thus gradually decreasing the slope of isotherms. The size of the surfactant molecule can decrease the adsorption and increasing the temperature will result in the desolvation of ethoxylated chains thus reducing the size and

increasing the adsorption. The solubility of the nonionic surfactant decreases by increasing the temperature thus increasing the adsorption. Beyond stage II the surface-surfactant interaction determines the adsorption which depends on the Hydrophilic Lipophilic Balance (HLB) of the surfactant molecules and the nature of the surface. At stage III and stage IV, surfactant-surfactant interaction plays an important role in adsorption. The alkyl groups tend to aggregate as the surfactant concentration approaches CMC which results in the vertical orientation of the surfactant molecule. The EO chain will be less coiled and more extended. The cohesive forces depend on the alkyl chain length, thus larger chains will have stronger cohesive forces thus increasing the adsorption. Subsequently, after stage IV interactions are very similar to that in bulk solution which results in aggregation forming micelles and hemi-micelles Figure 4-11. In Figure 4-11, sequence A represents weak interaction between the adsorbent and hydrophilic component of the surfactant, B represents the intermediate one and C represents a relatively strong interaction between the same [110]

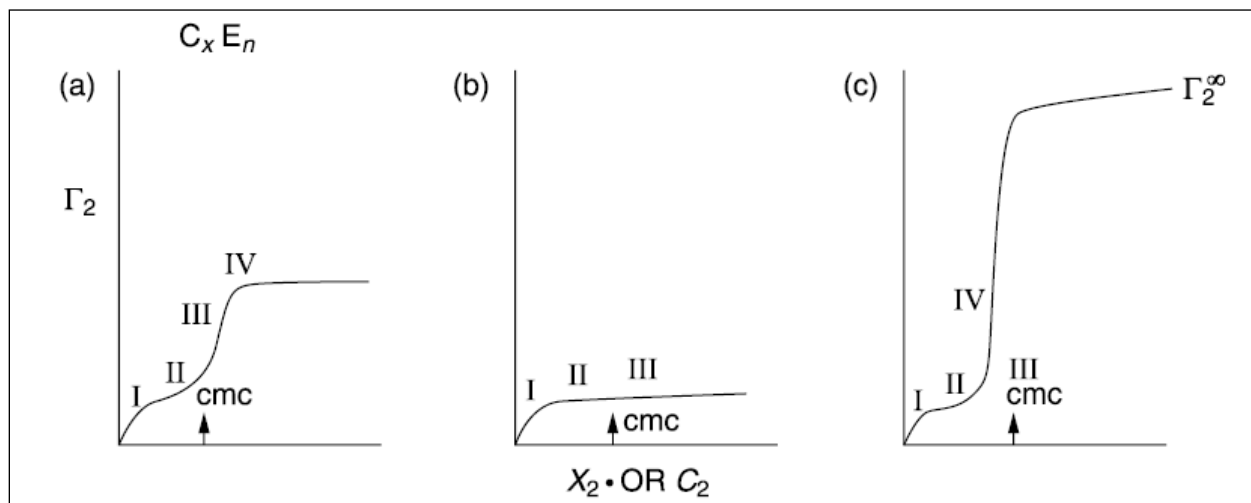


Figure 4-10: Adsorption isotherm for nonionic surfactant with sequences i,ii,iii corresponding in Figure 4-11.[110]

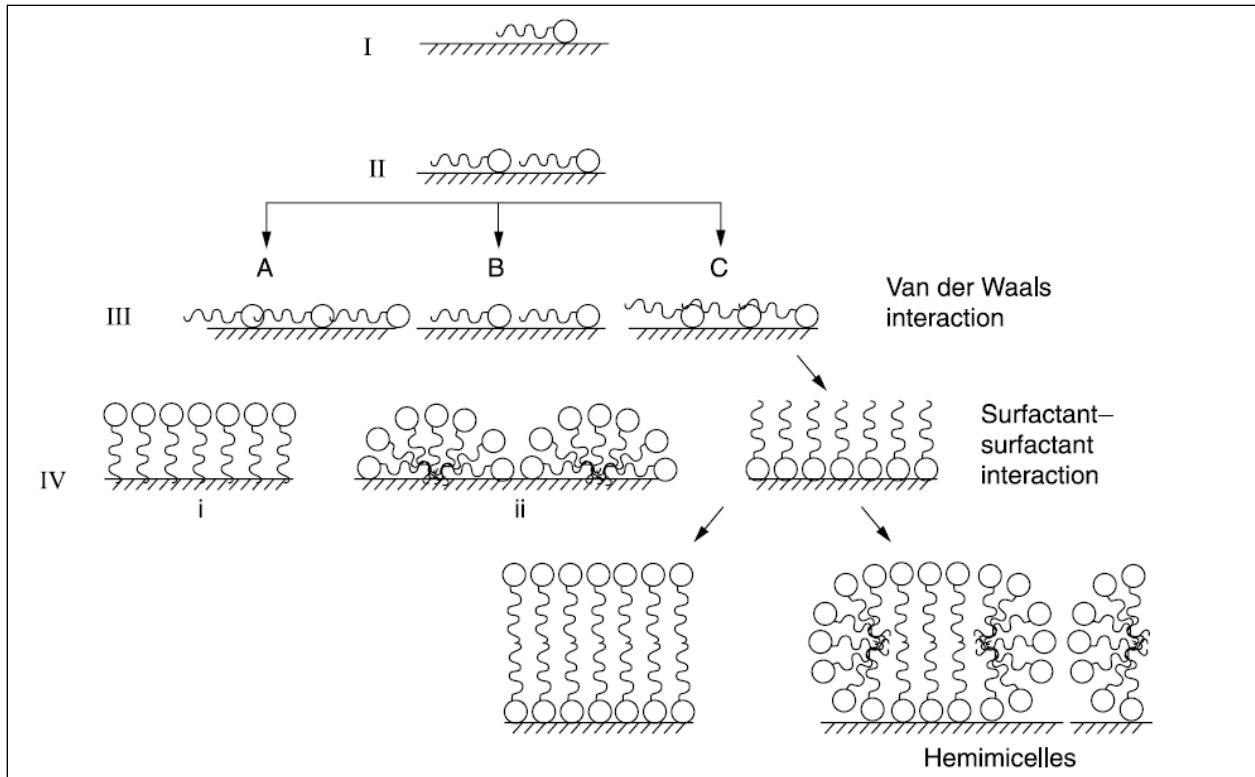
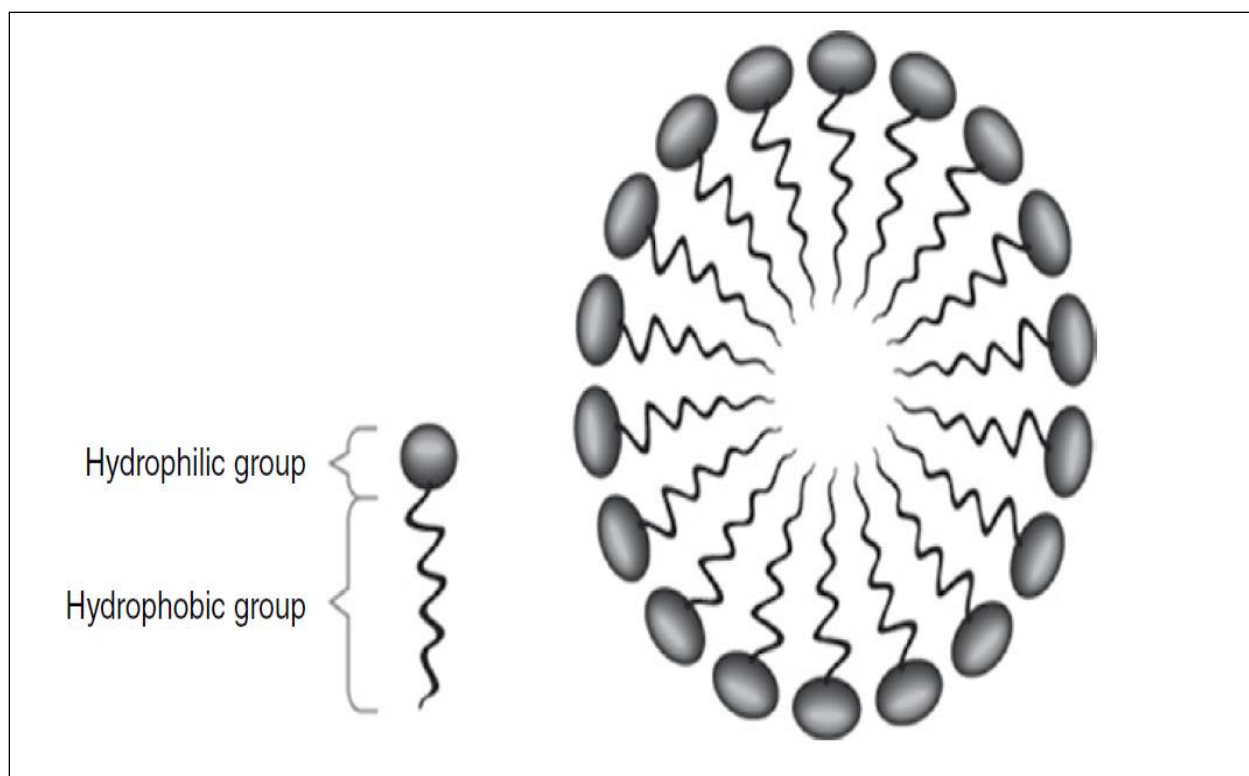


Figure 4-11: Schematic for the adsorption of nonionic surfactants to represent isotherm in Figure 4.10. [110]

#### 4.7 Critical Micelle concentration

The fundamental property of the surface-active agents is their tendency to form aggregates in the solutions. The aggregates initially formed are spherical and are called micelles (Figure 4-12).



*Figure 4-12: Micelle structure.[111]*

The physical properties of the surfactants are very similar to an electrolyte at low concentrations and change abruptly above a specific concentration known as critical micelle concentration (CMC) as shown in Figure 4-13. The exception for this is surface tension which decreases with an increase in the concentration of surfactants. At CMC all the surface-active ions or molecules associate in solution to form larger units that are called micelles. The most common technique of measuring CMC is by measuring surface tension which decreases till CMC and then remains constant. If we consider a graph of turbidity it increases with a steep slope after CMC which can be used as a visual test for confirming concentration above CMC. Nuclear Magnetic Resonance (NMR), fluorescence spectroscopy are other techniques that are used to measure physicochemical properties since micellization affects these properties. CMC depends on the chemical structure of the surfactant and it decreases with increasing alkyl chain length. The CMCs of nonionic surfactants are lower than ionic with the same alkyl chain length. The effects

of the head of the surfactant on CMC are moderate. Cationics have higher CMCs than anionics. The size of the head of the polar group affects CMC, an increase in size increases CMCs. Partial fluorination may increase CMC values, in the case of terminal methyl groups, CMC values approximately doubles [110][112].

Thus, from the application perspective for the washing of PPE, CMC plays a vital role. As the concentration approaches CMC, surface tension value decreases considerably which is beneficial in washing out hydrophobic contaminants. Similarly, above CMC the solubilization capacity of surfactants increases which needs to be considered while removing fireground contaminants.

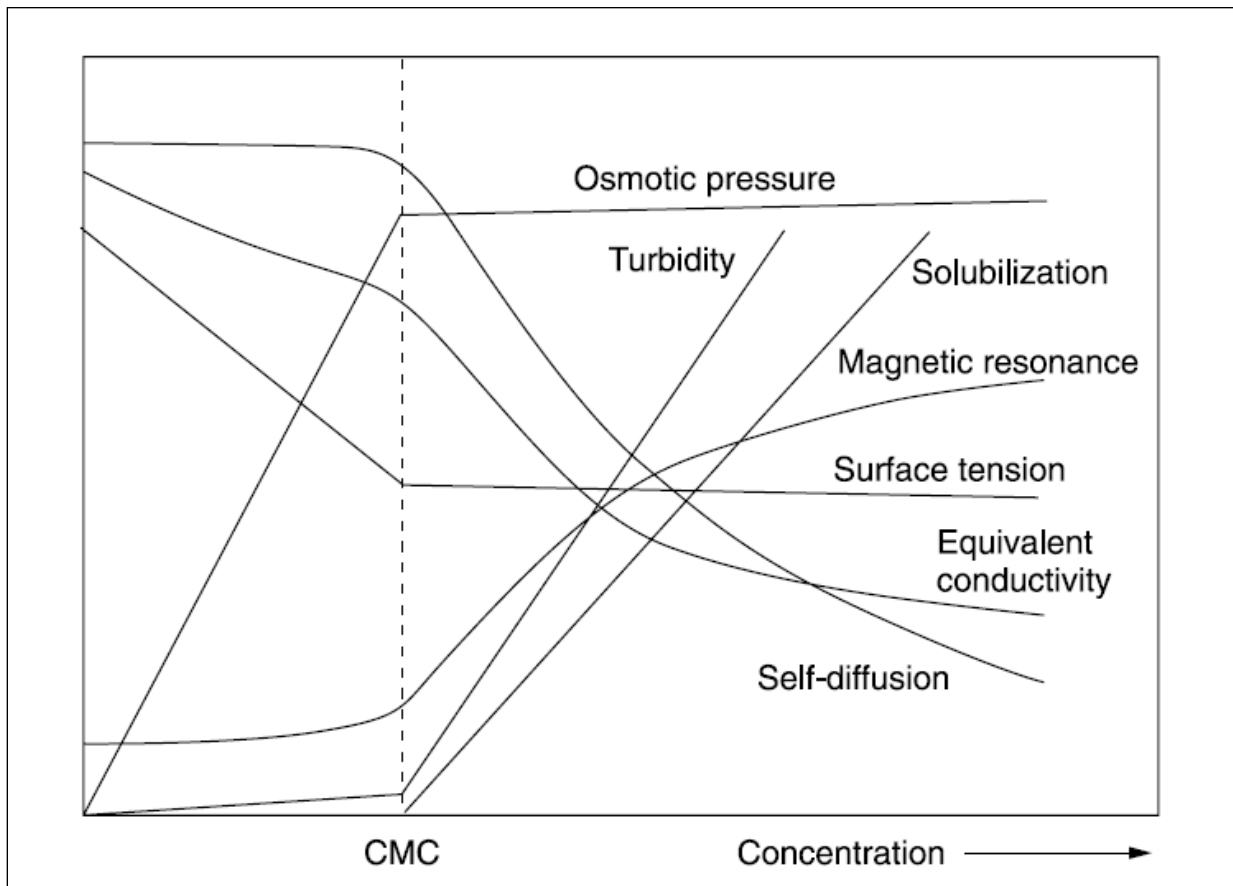


Figure 4-13: Physico-chemical properties dependence on the concentration of surfactants.[110]

#### 4.8 Temperature dependence of surfactants

The solubility-temperature relationship is often described as the Krafft phenomenon. The solubility of the ionic surfactant is very low at low temperatures and increases drastically (several orders of magnitude) over a narrow range of temperatures (Figure 4-14). The onset temperature at which this phenomenon starts is termed Krafft temperature. Minor changes in the surfactant's chemical structure may vary Krafft temperature [110].

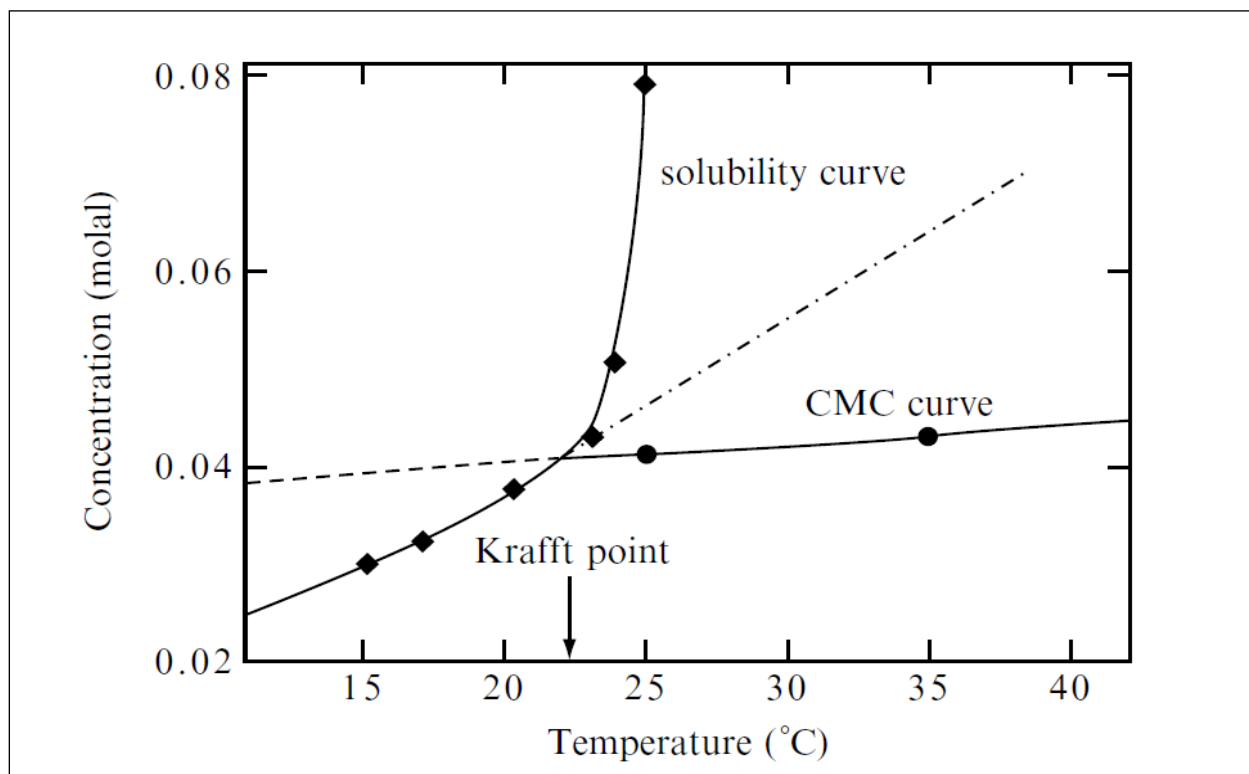


Figure 4-14: Temperature dependence of the solubility of the surfactant around Krafft point. [110]

An increase in the alkyl chain length increases the Krafft point and it can be reduced by introducing branching in the chains. The head group and counterion affect Krafft point, and adding salt increases the Krafft point. Adding the co-solvent reduces the Krafft point. Surfactants with ionic heads, compact highly polar heads and long alkyl chains have high Krafft temperatures. At Krafft, point solubility becomes equal to CMC and an equilibrium exists



between monomers, micelles and solid hydrated surfactant. For the region below CMC, solubility is low which limits the number of free ions in the solutions; and no micelles can be formed. As the solubility reaches CMC, micelles begin to form. To understand Kraft point, it is necessary to understand the energy relationships between the crystalline state and micelles. The variation in different micellar solutions is very low hence crystalline states in terms of packing state and ionic interactions are studied to understand the Krafft phenomenon [110].

Various techniques are used to lower the Krafft point of the surfactants. Generally, the modifications are done in the solid state to make the packing of hydrophobic chains in favor of the desired property. Modifications such as adding a methyl group to the branched alkyl chain, adding a polar group between an ionic head and alkyl chain, making the alkyl chains unsaturated (adding a double bond) are commonly practiced to lower the Krafft point [110].

This temperature dependence of properties of the surfactants highlights the importance of surfactants with low Krafft temperature. Thus, when considering solubilization a compromise is made while selecting a surfactant with an alkyl chain length. The longer alkyl chain length surfactant has low CMC values but higher Krafft temperature which indicates choosing an optimum chain length. Thus, increasing the temperature above the Krafft temperature may enhance the solubility of the surfactants. This highlights the importance of higher temperatures in cleaning PPE. The NFPA 1851 standard prohibits washing temperature above 40°C. Thus, washing PPE at a higher temperature may enhance the removal of fireground contaminants that need to be investigated.

#### 4.9 *Octanol-water partition coefficient*

Concepts of hydrophobicity and lipophilicity have a broader meaning in chemistry due to their importance in the environment. To study the bioavailability of any compound and its

distribution between soil and water it is important to consider the octanol-water partition coefficient. It can be defined as the ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase. The coefficient is denoted by  $K_{OW}$  and  $\log P$  [115]. The values of  $K_{OW}$  range in the orders of magnitude of  $10^X$  hence logarithmic value is taken to provide values in natural numbers. A higher  $\log P$  value indicates more partitioning in octanol hence greater hydrophobicity [115]. For example, the  $\log P$  value of benzyl butyl phthalate is 4.73 which gives us the value of  $5.3 \times 10^5$  [116].

$$\log P = \log \left( \frac{C_o}{C_w} \right)$$

*Equation 4-9: Octanol-water partition coefficient*

$C_o$  = concentration of compound in octanol and  $C_w$  = concentration of compound in water

The traditional methods use phase separation methods using a shake flask process that is tedious and require large amounts of pure compounds. Stir-flask, generator column, high-speed countercurrent chromatography method are some of the improvements in measuring  $K_{OW}$  [115].

The  $K_{OW}$  is a very important parameter to understand the affinity of the compounds to organic matter. The PAHs and phthalates have high  $K_{OW}$  values that indicate their behavior in water. This also justifies their high affinity towards organic matter and resistance to getting washed out. This, improving formulations that contain organic matter such as activated carbons, guar-gum, d-limonene, adding oily components, organic solvents such as hexane, heptane in the surfactant formulation will improve the removal of the fireground contaminants.

#### 4.10 ***Biosurfactants***

Biosurfactants are microbial surfactants that are produced extracellularly or as part of the cell membrane by bacteria, yeast, or fungi [113]. Biosurfactants are classified as glycolipids, lipopeptides, phospholipids, fatty acids, neutral lipids, polymeric and particulate compounds

(Table 4-1). Most of these groups are anionic or neutral. Only those who contain amine groups are cationic. The long-chain part of the fatty acids constitutes the hydrophobic nature of the molecule. Carboxylic acid, alcohol, amino acid, peptide is the hydrophilic nature of the molecule. The CMCs of the biosurfactants range between 1 to 200 mg/L. Biosurfactants have several advantages such as high specificity, low surface tension values, biodegradability, and biocompatibility.

Table 4-1: Different types of biosurfactants and their microbial origin.[113]

<b>Types of surfactants</b>	<b>Microorganism</b>
Trehalose lipids	<i>Arthrobacter parrafineus, Nocardia</i>
Rhamnolipids	<i>Pseudomonas aeruginosa, serratia rubidea</i>
Sophorose lipids	<i>Candida apicola, Candida bombicola</i>
Glycolipids	<i>Alcanivorax borkumensis, Arthrobacter sp</i>
Cellobiose lipids	<i>Ustilago maydis</i>
Polyol lipids	<i>Rhodotorula glutinus, rhodotorula graminus</i>
Lipopolysaccharides	<i>Acinetobacter calcoaceticus (RAG<sub>1</sub>), Pseudomonas sp</i>
Arthrofactin	<i>Arthrofacter</i>
Surfactin	<i>Bacillus subtilis, Bacillus pumilus</i>
Viscosin	<i>Pseudomonas fluorescens</i>
Lysine peptides	<i>Gluconbacter cerinus</i>
Phospholipids	<i>Acinetobacter sp</i>
Sulfonyl lipids	<i>T.thiooxidans</i>
Alasan	<i>Acinetobacter radioresistens</i>
Streptofactin	<i>Streptomyces tendae</i>
Particulate surfactant(PM)	<i>Pseudomonas marginalis</i>

Rhamnolipids are the group that has been studied extensively (Figure 4-15). *Pseudomonas aeruginosa* can process various organic groups containing C11 and C12 alkanes,

olive oil, glucose [117]. The surface tension value of 29 mN/m is the characteristic feature of this group. Fermentor, design, pH, nutrient composition, substrate, temperature are the factors that define yields and composition [113].

*Candida Bombicola* is a yeast that produces sophorolipids (Figure 4-16) from soyabean oil, glucose. Sophorolipids can lower the interfacial tensions of n-hexadecane and water to 5 mN/m with a small concentration of 10mg/L. This was consistent over the range of pH 6 to 9, temperatures from 20°C to 90°C.

Lipopeptides such as surfactin are produced by *Bacillus Subtilis* which is an amino acid-based surfactant. Surfactin is one of the most powerful biosurfactants which can reduce the surface tension to 27 mN/m with a very small concentration of 0.005% [113].

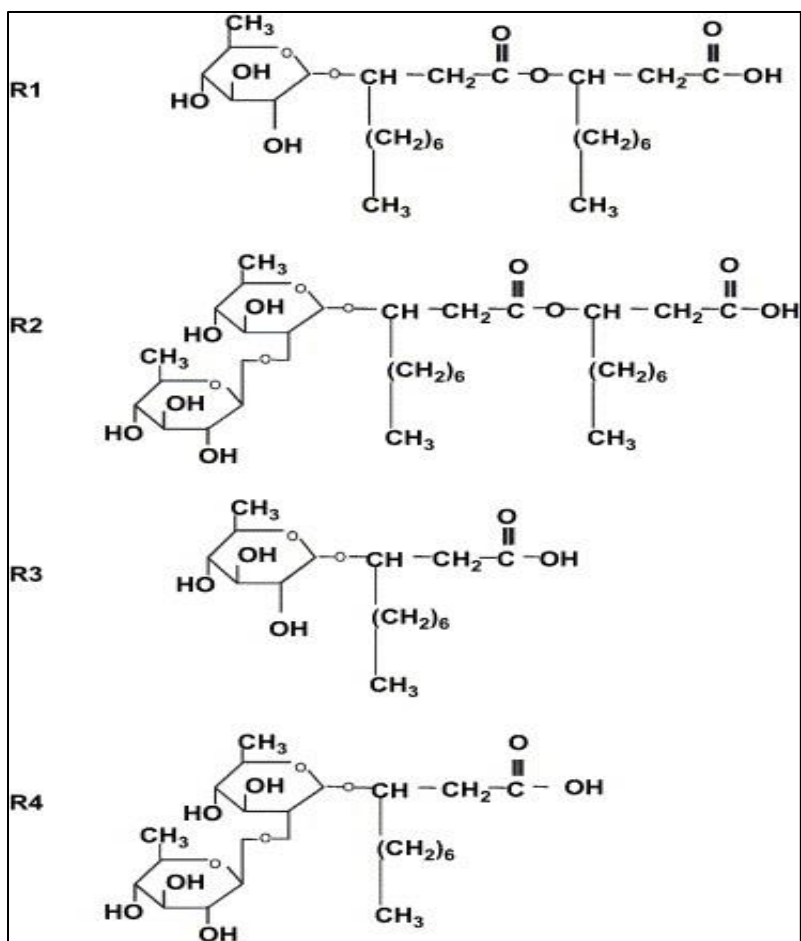


Figure 4-15: Structures of rhamnolipids produced by *Pseudomonas aeruginosa*. [113]

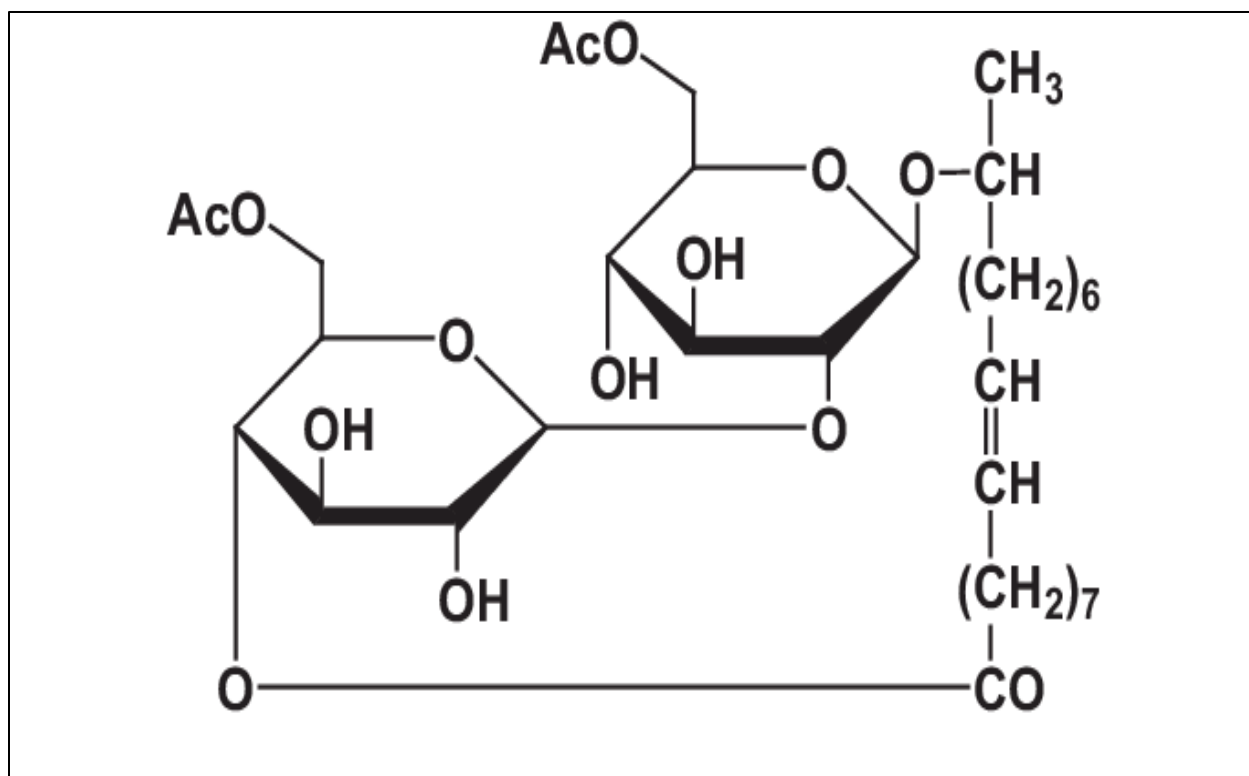


Figure 4-16: Structure of Sophorolipids.[113]

#### 4.10.1 Application of Biosurfactants

Biosurfactants are used in various sectors such as pharmaceuticals, the food industry, oil spill cleanup, oil recovery, etc. Due to the very nature of our research in removing hydrocarbons and other persistent contaminants, we will focus on some specific applications for biosurfactants.

##### 4.10.1.1 Enhanced oil recovery

Enhanced oil recovery (EOR) is a process (Figure 4-17) in which a displacing fluid is injected into the porous rocks to recover crude oil [118]. Biosurfactants are used in EOR applications and have been found very effective. They reduce the interfacial tension between oil and water in situ, viscosity of the oil more effectively than the conventional surfactants. Water flows without dislodging oil droplets from the rocks. When biosurfactants are introduced the microbes surround the oil droplets causing them to dislodge from the rocks and thus enhancing oil recovery [119]. A commercially available product Emulsan<sup>®</sup> is a polysaccharide-based

surfactant. Most of the surfactants are aerobic in nature although anaerobic surfactants such as *Bacillus licheniformis* JF-2 that is used in soil decontamination, EOR applications [120].

The formation of an oil-water emulsion increases the mobility until surfactant is adsorbed on the surface of the rocks. In an experiment conducted in Berea using Yates stock tank oil, EOR was obtained using biosurfactants. Rhamnolipids, sophorolipids, lipopeptides have great industrial significance and hence are produced on a larger scale. Also, the growth of the microbial colonies is exponential which makes it economically attractive for this application as compared to other chemical methods for EOR [119].

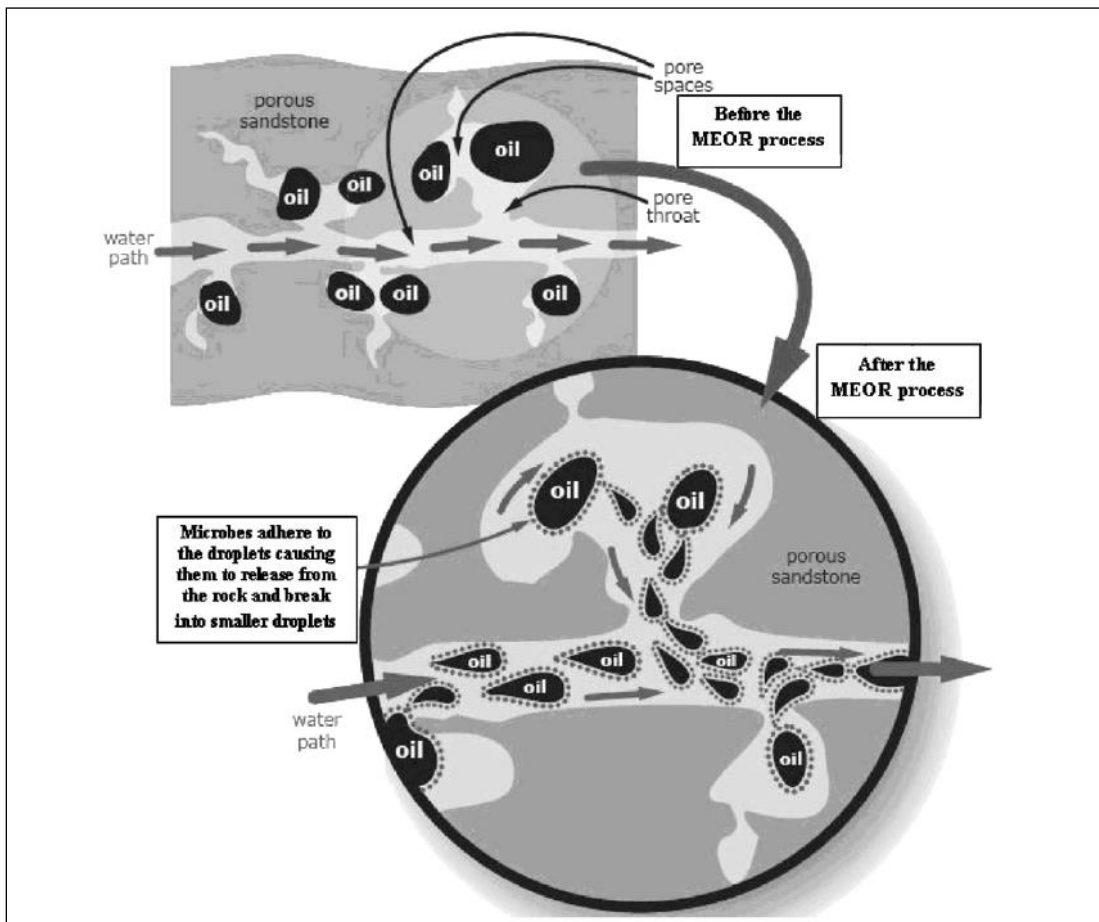


Figure 4-17: Process of microbial enhanced oil recovery.[119]

#### *4.10.1.2 Effect of biosurfactants on degrading contaminants*

##### *4.10.1.2.1 Application of Rhamnolipids*

###### *4.10.1.2.1.1 Petroleum Hydrocarbons*

Petroleum hydrocarbons have multiple constituents such as alkanes, cycloalkanes, polycyclic aromatic hydrocarbons. Multiple studies have shown that rhamnolipids are effective in degrading hydrocarbons such as hexadecane, octadecane, n-paraffin, phenanthrene [121]. Rhamnolipids enhanced solubility of the substrate increasing the hydrophobicity of the surface to associate hydrophobic surface more easily [122]. With a small concentration of 300mg/L, rhamnolipids increased the demineralization of octadecane from 5% to 20% [123]. *P.aeruginosa* degraded hexadecane effectively. For a petroleum sludge, rhamnolipids were effective in remediating alkanes (more than 90% for alkane with small chains) and showed significant results for longer chain alkanes [124].

###### *4.10.1.2.1.2 Polycyclic aromatic hydrocarbons*

PAHs are persistent organic pollutants that are found in petroleum refining, structural and wildland fires, coke production. Studies have shown that naphthalene demonstrated better solubility with rhamnolipids (30 times more) as compared to SDS and a non-ionic surfactant (Triton X-100). One of the major disadvantages of the procedure was the time required for solubilization 40 days for biosurfactant as compared to Triton X-100: 100 hours [125]. Different researchers have used different strains of rhamnolipids to degrade PAHs which were found to be more effective than the conventional surfactants. Phenanthrene was degraded more easily using rhamnolipids [126]. The bioremediation of contaminants such as PAHs and benzo[a]pyrene (BaP) was enhanced using *Pseudomonas aeruginosa* in the bioaugmentation process [127].



#### 4.10.1.2.1.3 Oil

Rhamnolipids surfactants have been used to enhance the release of the low solubility compounds from soil. These surfactants were able to wash out the oil three times more effectively than water from the beaches in Alaska after the Exxon Valdez oil spill [122]. A concentration as low as 1% is required to get adsorbed on the oil-water interface to degrade hydrocarbons [128]. Oil spill cleanup using biosurfactant from the sand was studied using rhamnolipids which decreased the interfacial tension between heptane and water to as low as 0.01mN/m. The surface tension of water in the process was 29 mN/m [129].

#### 4.10.1.2.2 Application of Sophorolipids

Very limited literature is available on Sophorolipids application in bioremediation. Sophorolipids have been used to remove heavy metals from metal contaminated soils [130]. Phenanthrene was degraded in a 10% soil suspension and its concentration decreased from 80 mg/L to 0.5 mg/L in the presence of 500 mg/L of the surfactant [131]. The North Dakota Beulah Zap lignite coal was partially solubilized using a crude preparation of *Candida bombicola* that produced sophorolipids.

#### 4.10.1.2.3 Application of surfactin

Although surfactin is considered to be one of the powerful biosurfactants, very few studies have been performed on the environmental application of surfactin. The strain from *Bacillus subtilis* was used for in-situ removal of oil. The results showed an oil removal efficiency of 62% [122]. Even low concentrations of surfactin (0.25% in 1% NaOH) were able to remove metals such as copper (25% removal efficiency), 6% zinc from the soils and sediments. Consecutive washing of soil with 0.25% surfactin was able to remove 70% of the copper and 22% of the zinc. The mechanism to remove metals from the surface was simple. Surfactin was

able to adsorb at the soil interfaces to form metal complexes and then lowering the interfacial soil-water tension and fluid forces thus resulting in the desorption of metals [132]

Biosurfactants have shown immense potential in the remediation of both organic and inorganic contaminants via desorption and biodegradation mechanism. Their low toxicity, bioavailability make them a very promising option in resolving environmental issues. Incorporating biosurfactants in a formulation can help in improving the removal of contaminants especially PAHs from PPE. Their activity decreases surface tension values to less than 50% of its original surface tension which makes a huge impact on the mobility of these hydrophobic compounds in water. One of the limitations of this option is the long process time. Although the longer durations may affect the practicality of these compounds, they can be considered to be used in the pretreatment of PPE.

## Chapter 5: The Sublime Art of Pressurized CO<sub>2</sub> and its applications

Environmental awareness has increased in the past decade. Perchloroethylene (PERC) has been used by professional dry cleaners for decades. With the growing concerns about its toxicity, several alternatives such as hydrocarbons, acetal, Green Earth<sup>®</sup> have been used. Table 5-1 illustrates some of the solvents that have been used in dry cleaning.

*Table 5-1: Solvents used in dry cleaning and their environmental and health effects.[133]*

<b>Solvent</b>	<b>Environmental impacts</b>	<b>Potential human impacts</b>
Perchloroethylene	Persistent in water, soil, air, sediment, aquatic toxicity	Irritates skin, damage to the central nervous system
DrySolv <sup>®</sup> n-Propyl Bromide	Very persistent in air, soil and toxic to the aquatic environment	Damage to the central nervous system, reproductive system, kidney, liver
DF-2000 fluid	Highly flammable, persistent in air, soil	Bioaccumulation, irritation to eyes, skin, respiratory tract
Sasol LPA 142	Toxic to the aquatic environment	Irritation to eyes, skin, respiratory tract
Siloxane D5 (GreenEarth <sup>®</sup> )	Very persistent in air, soil and toxic to the aquatic environment	Probable carcinogen, reproductive toxin, damage to the liver, immune and central nervous system, mild irritation to the eyes.

A growing interest is generally observed in producing “clean” technologies that have fewer environmental concerns like low toxicity, reduced energy consumption, etc. Such necessities gave birth to high-pressure technology. Supercritical fluids (SCF) and liquid CO<sub>2</sub> are

interesting corollary of this high-pressure technology. SCFs are substances that have temperature and pressure values above critical values (Figure 5-1). While subcritical fluids act in slightly lower pressure regions, supercritical fluids have an excellent combination of properties: gas-like viscosity and diffusivity along with liquid-like density and solvating properties. These properties make SCF an excellent solvent for numerous applications. The phase behavior of SCF can be demonstrated using an autoclave visual representation. In Figure 5-2 (a), a clearly defined meniscus can be seen in a two-phase equilibrium. When temperature and pressure are increased, the meniscus is less well defined since the difference in the densities of the phases decreases. Figure 5-2 (b), Figure 5-2 (c) represents a homogenous system [134].

Supercritical fluids like CO<sub>2</sub> (scCO<sub>2</sub>) are non-toxic, non-carcinogenic, non-mutagenic, non-flammable, and thermodynamically stable. Also, its thermophysical properties like viscosity, diffusivity, density can be readjusted by simply varying the operating temperature and pressure. Hence it is called “Green-Solvent” [135] [136] [137]. SCFs are a great alternative to other fluids like fluorocarbons, sulfur dioxide, perchloroethylene, etc. Due to numerous such advantages, SCFs are used in industries like pharmaceuticals, the food industry, textiles, etc [133]. The scCO<sub>2</sub> and liquid CO<sub>2</sub> are not intrinsically different even though they have significant discontinuities in physical properties [138]. Thus, the basic mechanism of removing contaminants is very similar for both solvents.

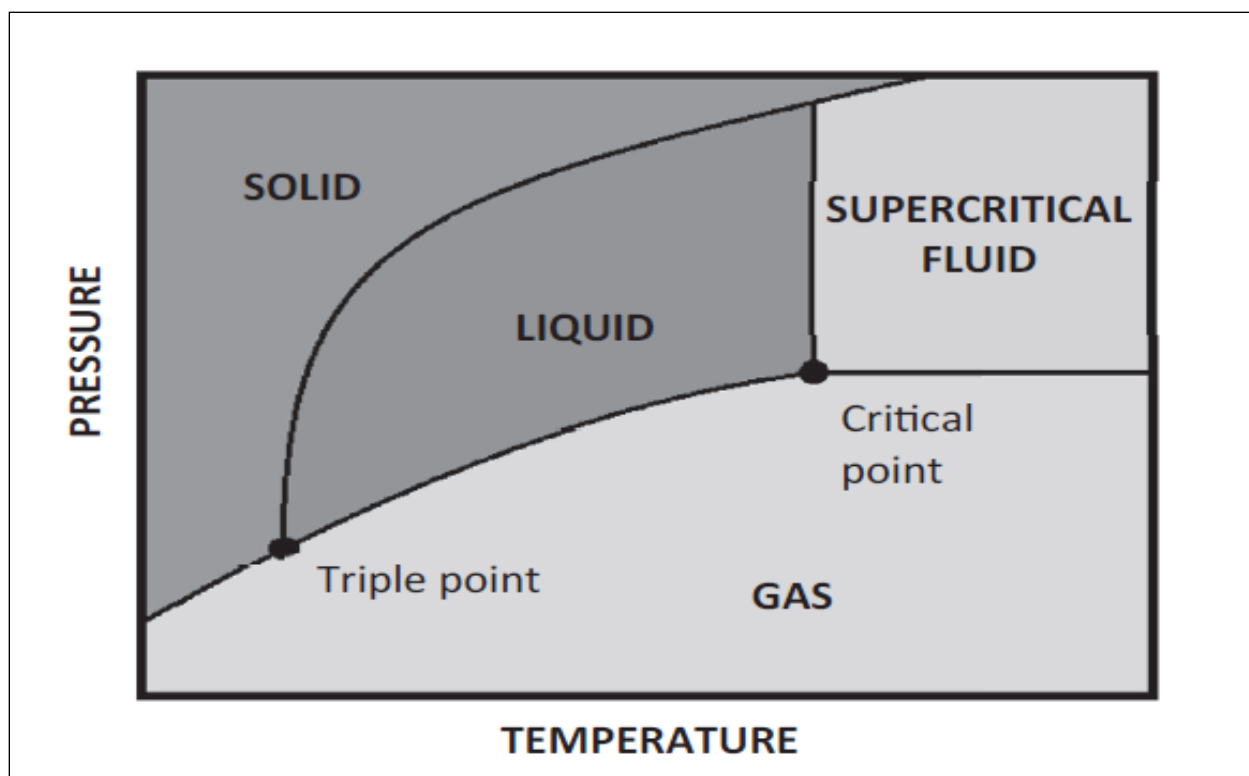


Figure 5-1:Phase Diagram.[133]

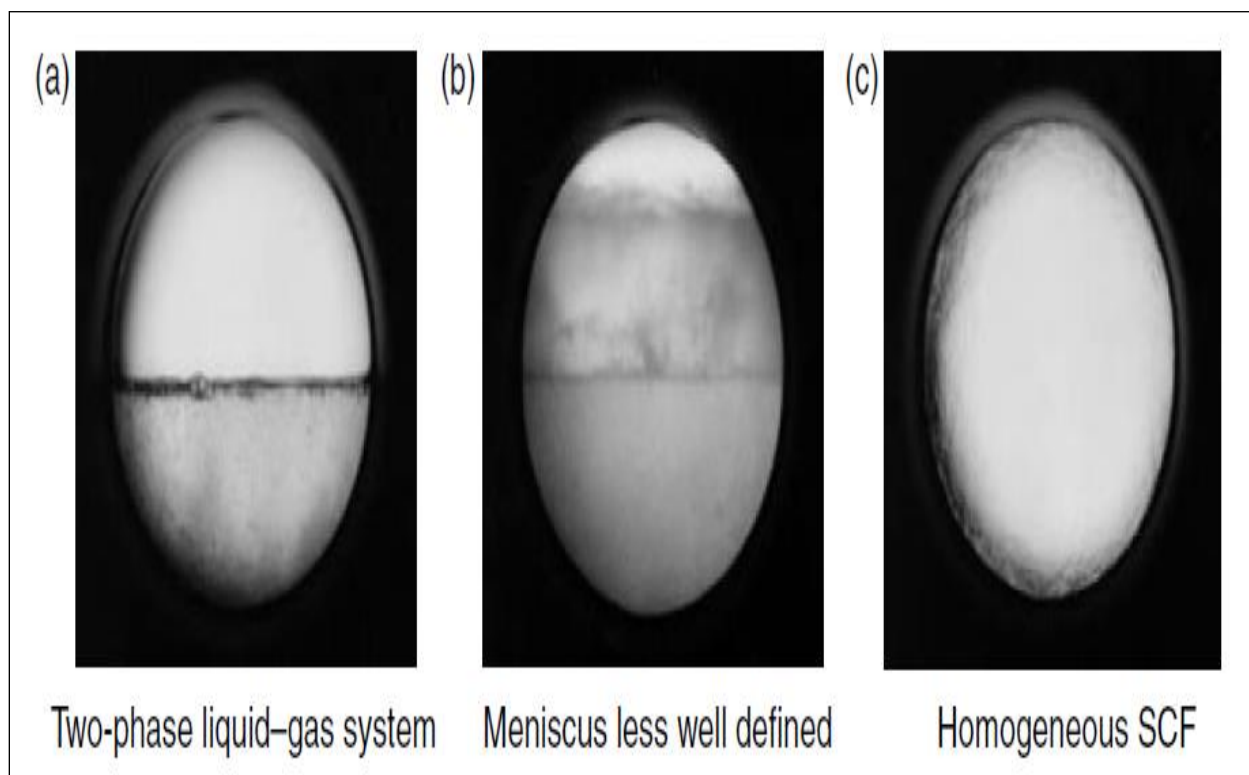


Figure 5-2:Autoclave visual representation of SCF.[134]

CO<sub>2</sub> molecules have a linear structure and hence no dipole moment which induces low polarizability. This results in a low zero frequency dielectric constant and a low Hamaker constant. The density of liquid CO<sub>2</sub> is around 850-900 kg m<sup>-3</sup> at the operating conditions for dry cleaning. Figure 5-3 illustrates some of the physio-chemical properties of liquid CO<sub>2</sub> as a function of density. Interfacial properties need to be considered for dry cleaning applications. The surface tension of liquid CO<sub>2</sub> has been reported to vary from 16.5 to 0.59 mN/m for a temperature range of -52°C to 25°C. The highlighted region demonstrates the surface tension values for dry cleaning applications: ~3-4 mN/m [139].

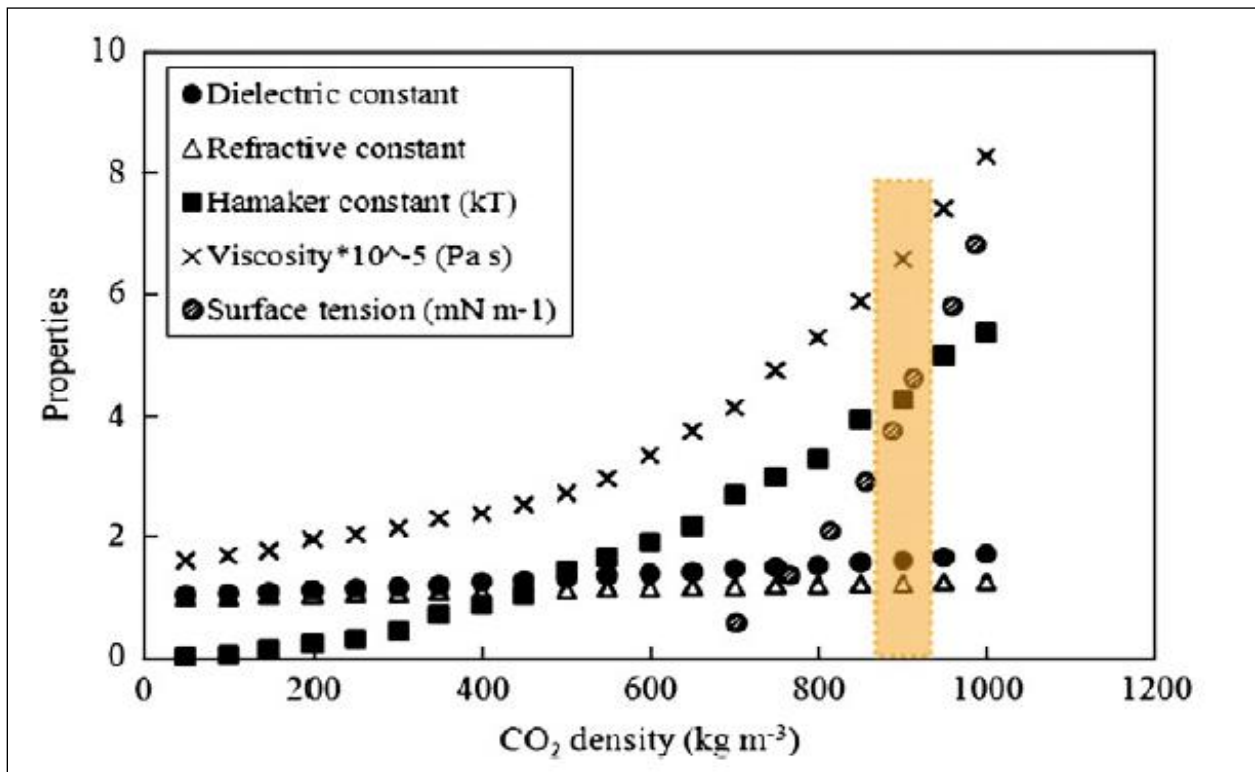


Figure 5-3: Physiochemical properties of liquid CO<sub>2</sub> with a change in density. Yellow marked region indicates the operational area for dry cleaning application.[139]

The Van der Waal interaction energy parameter is a function of the distance between a substrate and particle and compares the values for Van der Waal interaction for three different solvents: PERC, water, and liquid CO<sub>2</sub> (Figure 5-4). The interaction energy increases with

distance  $d$  for liquid CO<sub>2</sub> in liquid medium as compared to PERC thus indicating limited solvent properties for the liquid CO<sub>2</sub> [139].

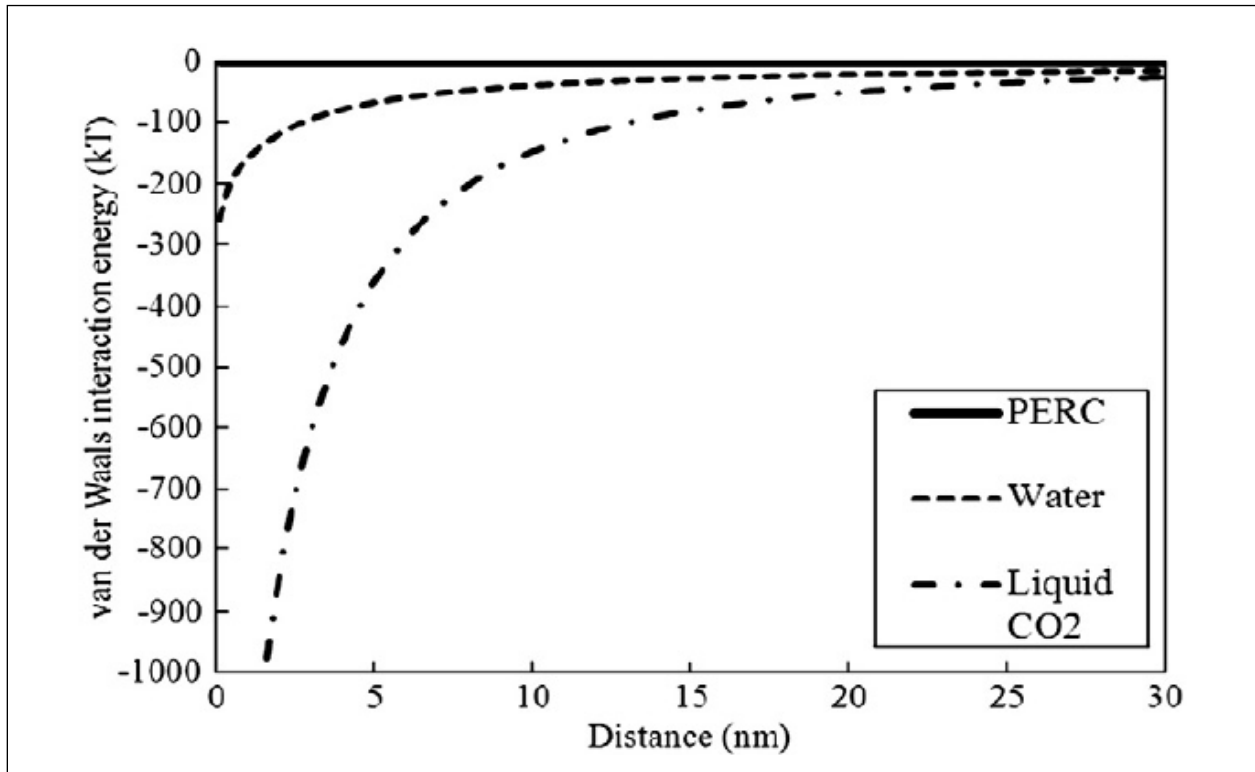


Figure 5-4: Van der Waal interaction between soil particle and substrate as a function of  $d$  in different solvents.[139]

### 5.1 Supercritical State [140]

Supercritical fluids have a density that is only 30% of a normal fluid which makes SCFs a good solvent along with high diffusivity and rapid mass transfer. In practical applications, the operating temperature is not significantly above the critical temperature ( $T_c$ ). Generally, Guldberg's rule is used to predict the solvent characteristics of a low boiling substance in its supercritical state to compare boiling temperature  $T_b$  and  $T_c$ .

$T_b = \left(\frac{2}{3}\right) \times T_c$	<i>Equation 5-1: Guldberg's Rule</i>
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Density is an important parameter in the SCFs application hence the critical point region should be considered for temperature and pressure as the rate of change of density is highest near the critical point. Small changes in pressure can have a significant impact on density. Solvent properties improve with the fluid density and thus pressure can strongly influence the solvent properties. The ideal gas equation can be used to determine the relationship between fluid pressure and density which can be used to measure and control the density.

$$PV/RT=1, V = \text{molar volume and } \rho = \text{mass density} = M/V$$

For higher density supercritical fluid, we have to introduce compressibility factor= $z$

$$PV/RT=Z$$

Above critical pressure (350 bar), solvent power increases exponentially with a small increase in pressure. The effect of temperature is more complicated: for the region below 350 bar, density decreases with an increase in temperature along with a decrease in solubility. When non-polar mixtures are considered like oily surfaces, cleaning efficiencies improve from regions of 200 to 270 bar. Increasing the pressure above 270 bar will increase the solubility of CO<sub>2</sub>. But diffusivity of CO<sub>2</sub> increases at higher pressure which might affect redeposition.



Table 5-2: Solvents and their critical parameters.[141]

Fluid	Molecular weight	Density gm/mol	Critical Temperature (°K)	Critical Pressure (bar)
Methanol	32.04	0.791	513.1	80.9
n-Hexane	86.18	0.659	507.4	30.1
isopropanol	60.10	0.786	508.8	47.6
Carbon dioxide	44.01	0.476	304.2	73.8
Acetonitrile	41.05	0.782	548.0	48.3
Acetone	58.08	0.790	508.1	47

### 5.2 Hildebrand Solubility Parameter

Hildebrand solubility parameter  $\delta$  is related to the thermodynamic properties of dense gases. Solubility parameter  $\delta$  is a semi-quantitative entity calculated in calories per cubic centimeter [140] [142].

$\delta = \frac{\left(1.25 P_c \frac{1}{2} \rho_r\right)}{\rho_r(\text{liq})}$	<i>Equation 5-2: Hildebrand Solubility Parameter</i>
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$P_c$  is the critical pressure,  $\rho_r$  is the reduced density, and  $\rho_r(\text{liq})$  is the reduced density of the liquid. Reduced density is the ratio of supercritical density at a given pressure and temperature to critical density  $\rho_c$

$$\rho_r = \rho / \rho_c$$

### 5.3 Solubility in Supercritical Fluid Cleaning

Solubility is the maximum amount of solute that can be dissolved in a solvent. In simple terms, this concept is often called as *like dissolves like*. Thus, polar compounds dissolve effectively in polar solvents and non-polar compounds dissolve in non-polar solvents. From the application point of view for cleaning, the type of soil and final cleanliness are key parameters in determining the cleaning method. The fireground contaminants that were presented in Chapter 3: were identified as non-polar and hydrophobic mostly. This makes the choice of solvent crucial for our research. For a very long-time, chlorofluorocarbon solvents like Freon-113 were used in the removal of greases, oils, etc. Fluorocarbons have been banned due to environmental issues. Supercritical carbon dioxide is an effective replacement for fluorocarbons as a solvent. The extractive power of CO<sub>2</sub> increases manifold as its density is increased by increasing the pressure. Thus, the solubility of numerous organic compounds increases in carbon dioxide with an increase in density. For dry cleaning operations, the liquid state of CO<sub>2</sub> is preferred over the supercritical state since the two-phase gas-liquid interface is beneficial in trapping soil particles. CO<sub>2</sub> at 20°C and equilibrium pressure of 56 atm (56.742 bar) acts as a very good solvent. Hence, when SCF is considered as a solvent for cleaning we need to consider the solubility of that compound in SCF. At such times parameters like Hildebrand solubility can help us in determining the cleaning model. The solvating power of SCF is a function of its density which depends on pressure. Temperature is an important factor that needs to be taken into consideration when volatile compounds are present. In a cleaning system when the temperature is increased, the density of the solvent decreases but the volatility of a contaminant increases which facilitates the cleaning process. The solubility of a compound in a liquid is dependent on the heat of fusion  $\Delta H_f$ .

$$\ln(x) = \Delta H_f / R (1/T_f - 1/T)$$

*Equation 5-3: Heat of fusion*

$x$ = mole fraction of solute,  $T_f$ = melting point of solute,  $T$ = temperature of the solution.

The assumptions for this equation include:

Changes in volume at different temperatures and heat capacities are negligible.

Only dispersion force is present between a solute and a solvent.

Figure 5-5 represents a schematic of the solubility of a compound. For segment A-B, solubility decreases as the compound are diluted by a fluid. When pressure is increased for the B-C segment, solubility increases as pressure is increased above the threshold pressure. For segment C-D when pressure is further increased solubility decreases due to repulsive forces that squeeze out solute from the solution. Segment D-E is more specific for volatile contaminants where an increase in pressure can increase the solubility [143].

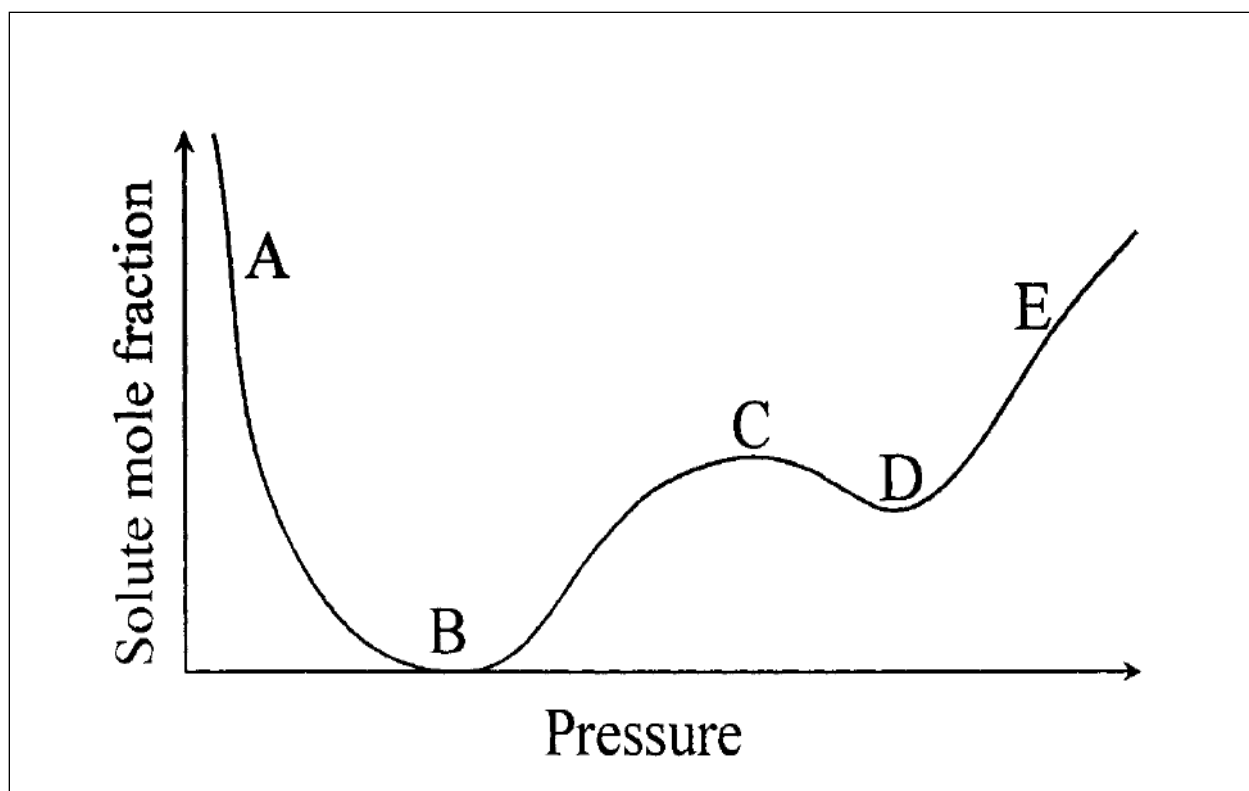


Figure 5-5:Compound solubility in SCF as a function of pressure.[143]

#### 5.4 Enhancement of the solubilities of CO<sub>2</sub>

Solubility of sc-CO<sub>2</sub> can be increased in several ways:

- Modifying a solute
- Adding a co-solvent
- Increasing the bulk density of the sc-CO<sub>2</sub>

Modification of a solute is a very common approach where the solute is made more CO<sub>2</sub>-philic. Molecules with long hydrocarbon chains have a higher solubility than aromatic or polar substrates except for fluorocarbons and siloxanes. Although the reason for such behavior has not been clear, nuclear magnetic resonance (NMR) and computational chemistry speculated an increase in solute-solvent Van der Waals interactions due to fluorocarbons. The co-solvent is generally added to modify the sc-CO<sub>2</sub> properties and act more like the substrate. Solvents such as

methanol, toluene, hexane can be added to tune the polarity or an affinity for aromatic species. Thus, the addition of the co-solvent deviates sc-CO<sub>2</sub> from being an ideal green solvent because sc-CO<sub>2</sub> can be recovered by depressurizing and then collecting it separately while the co-solvent is released into the environment [134].

### 5.5 *Partition coefficient*

The partition coefficient is defined as the concentration of a contaminant on the surface [ $C_s$ ] to the concentration of the contaminant in the SCF solvent [ $C_F$ ]. We can demonstrate the distribution behavior of a contaminant between solvent and surface by plotting [ $C_s$ ] as a function of [ $C_F$ ] as shown in Figure 5-6. Initially, the value of [ $C_s$ ] is high, and as the cleaning progresses, [ $C_s$ ] decreases as [ $C_F$ ] increases. Line C represents an ideal state where the partition coefficient is constant over a wide range of concentrations of the contaminant. Generally, curve A or B is observed. Curve A is observed when the concentration of contaminants in solution is related to the amount absorbed onto a surface and is thought of as an adsorption isotherm. Curve B is the case when a contaminant has limited solubility in the solvent or dissolution of the contaminant is limited by surface interactions [143].

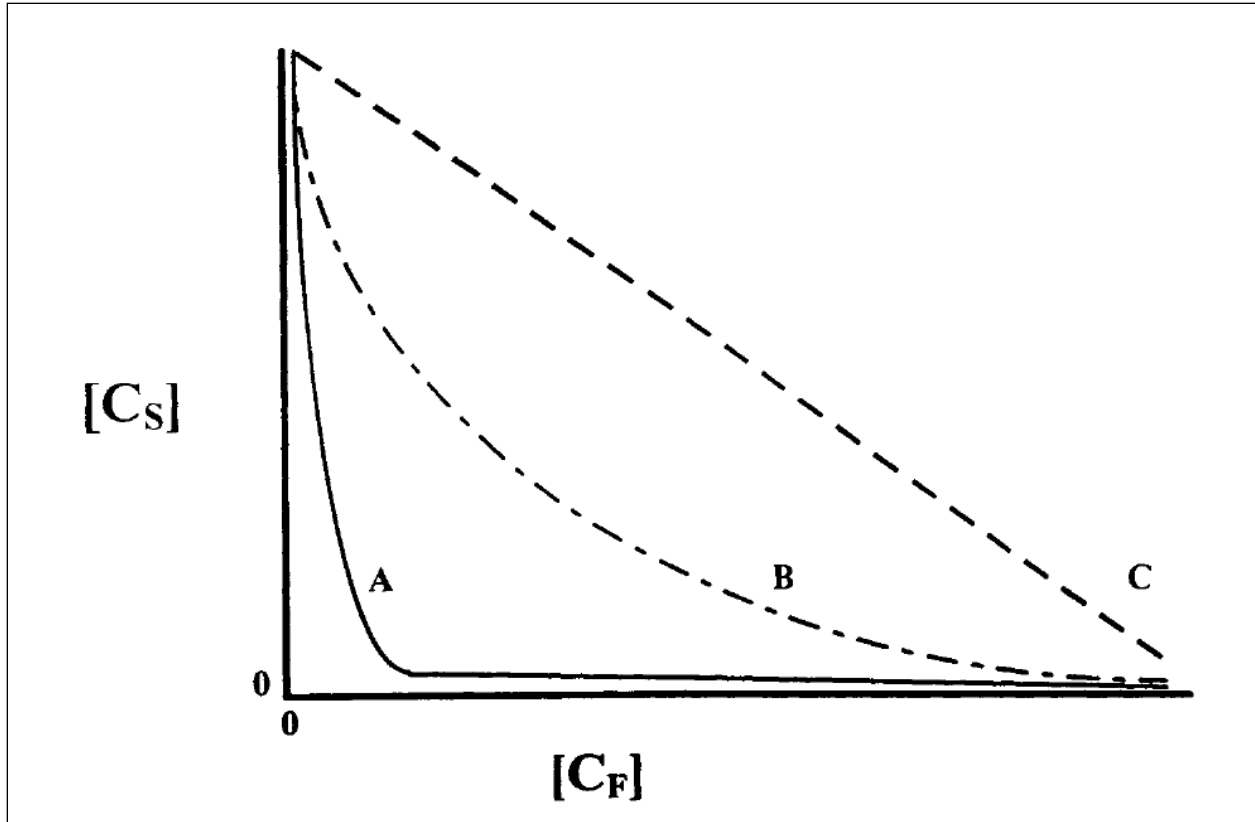


Figure 5-6: Plot of partition coefficient as a function of the surface,  $[C_s]$  and fluid,  $[C_f]$ , concentrations.[143]

Contaminant partitioning occurs back and forth and between phases, hence they are expressed in terms of equilibrium concentrations. Solubility is related to contaminant vapor pressure and temperature thus, increasing the temperature increases the partitioning into the fluid which helps in better removal of contaminants. Figure 5-7 indicates a simplified model for the effective removal of contaminants in a supercritical fluid. The diffusion coefficient  $D$  is an important parameter that needs to be taken into consideration which encompasses molecular motion when a molecule moves from a highly concentrated region to a low concentrated region.  $P_{SF}$  corresponds to the partition coefficient from 'surface to SCF'. Thus,  $P_{LF}$  corresponds to the partitioning of the contaminant from the bulk phase (includes both solid and liquid) and cleaning solvent. Subscripts  $S$  indicates surface,  $L$  for a contaminant, and  $F$  for SCF. For effective

contaminant removal, the contaminant must be present in the bulk flow of the supercritical solvent. This is a multistep process:

1. Partitioning occurs from the substrate surface into the bulk liquid of the contaminant after which the contaminant then diffuses to the surface in contact with the cleaning solvent represented as  $D_L$ . Contaminant partitions into the fluid phase of the boundary layer.
2. The boundary layer is a solvent layer that has a high viscosity and the non-flowing solvent is in contact with the cleaning surface and the contaminant. The contaminant to be removed from the surface must diffuse from the surface through the boundary layer and into the bulk flow  $D_f$ .
3. Supercritical extraction processes do not experience mass transfer limitations because they have gas-like diffusivities which are several order magnitudes higher than liquids. Hence extractions in SCF are highly efficient in cleaning.
4. The thickness of the boundary layer is very important for contaminant removal. If the boundary layer is thick, diffusion of the contaminant into the bulk solvent layer is slow that can lead to a slow dissolution process. The static dissolution where no flow is occurring within the cleaning chamber is a good example of this. The boundary layer in this case is essentially a bulk solvent and once the solvent becomes saturated with the contaminant, dissolution or extraction of the contaminant is stopped. If the boundary layers are thin and the solvent flow is dynamic cleaning occurs rapidly due to the fast diffusion of the contaminant across the boundary layer. Thus, the flow of the solvent across the surface needs to be maximized.

The above mechanism for the removal of the contaminant presents an ideal scenario for removing the particle adsorbed onto the surface of the different layers of PPE. The octanol-water

partition coefficient of the phthalates and PAHs, in particular, demonstrated the low partitioning in water. This can be remedied by using a pressurized solvent such as liquid CO<sub>2</sub> that can improve partitioning in the cleaning solvent improving the desorption of these contaminants from the fabric surface.

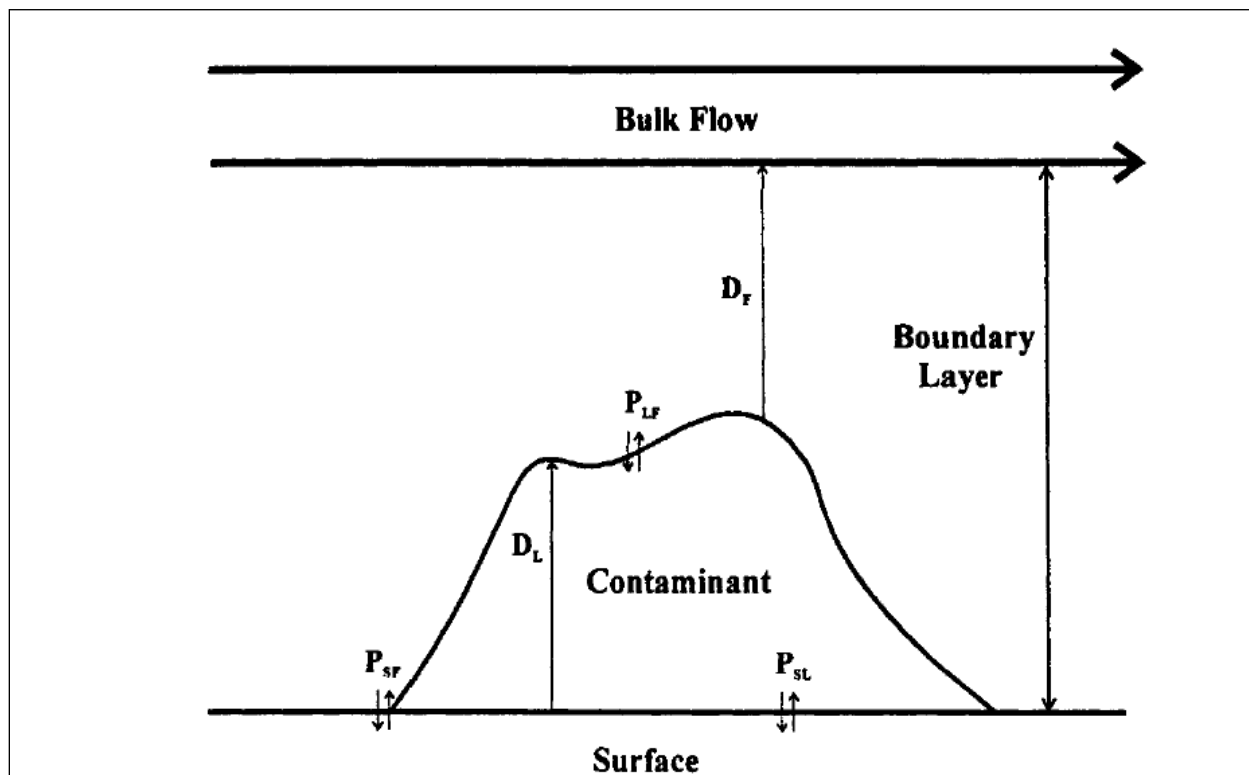


Figure 5-7: Model for removal of a contaminant in a supercritical fluid.[143]

Removing contaminants from the surface can be difficult. When trying to dislodge contaminants, physical sorption plays a much significant role than chemical sorption. Supercritical fluids have lower viscosities and surface tension values than conventional liquid solvents. This makes them superior to the conventional liquid solvents where the contaminants can be dislodged in crevices or physical barriers. This results in the complete removal of the contaminant. This will occur if the contaminant is completely soluble and partitions to the bulk SCF flow. When considering the three layers of the PPE, the moisture barrier is the most difficult layer to clean due to the limited mobility of the water, membrane, and sensitive non-woven

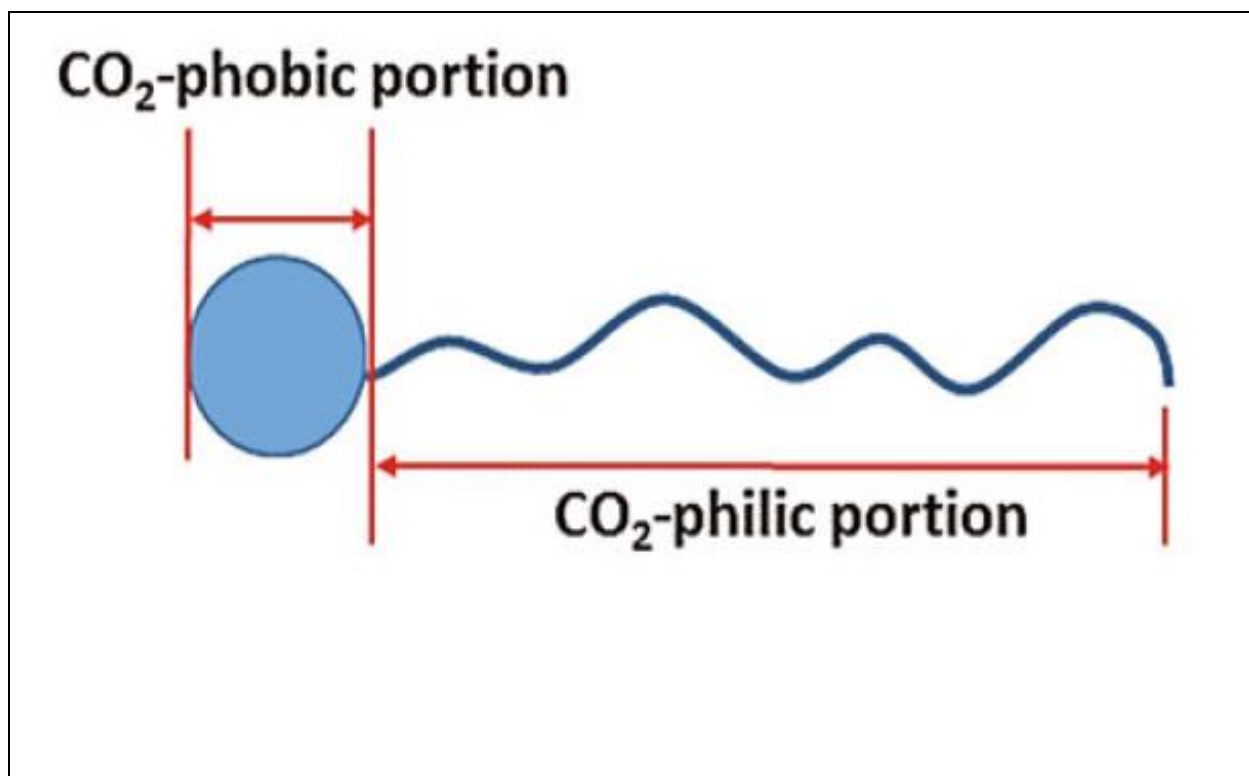


batting. Thus, dislodging contaminants from this garment can be difficult during conventional washing. The lower viscosities of pressurized CO<sub>2</sub> can be a major advantage in cleaning out the moisture barrier specifically. The outer shell of the PPE has water and oil repellent finishes applied. Thus, having a cleaning solvent like CO<sub>2</sub> that has low surface tension and non-polarity can have an added advantage in cleaning the PPE of the contaminants. Higher turbulence is required to remove less soluble contaminants. The final stage in the cleaning is the separation process where the contaminant is removed from the solvent. In the separator, the used solvent is passed through the cleaning chamber into a vessel where it is expanded into a gas. The extracted compounds are collected in the separator and the gaseous solvent is passed back into the flow stream where it can be reused. If the contaminant is miscible with the fluid and has high vapor pressure, the contaminant can get carried over into the solvent reservoir. The removal of volatile contaminants from the solvent is very difficult from an operational point of view [143]. This is a critical point in the application of pressurized CO<sub>2</sub> for cleaning PPE. Our primary focus is on removing contaminants that are semi-volatile in nature from PPE. The prevention of contamination of the solvent is necessary to prevent cross-contamination of the PPE. To avoid such contamination in the cleaning medium using a scavenger textile material or commonly called “sacrificial material” such as cellulose-based fabrics like cotton, cotton-terrycloth, cotton-velveteen will improve the filtration of contaminants from the cleaning medium (here CO<sub>2</sub>) [144]

### 5.6 CO<sub>2</sub>-philic surfactants

Supercritical solvents are very attractive solvents due to growing environmental concerns due to their unique physical properties. Supercritical CO<sub>2</sub> is the most versatile, benign, and inexpensive solvent as compared to other conventional solvents. In textile cleaning, liquid CO<sub>2</sub>

has been able to remove various compounds that include grease, fatty substances, non-polar compounds, and fairly remove polar compounds with very little added water [145]. The polar soils are not efficiently removed because liquid CO<sub>2</sub> is non-polar, and its physical properties make poor dispersion of particulate matter. Liquid CO<sub>2</sub> has a low dielectric constant which makes the textile-particle interactions such as Van der Waal forces relatively stronger than in perchloroethylene. Also, due to low viscosity, the mechanical forces exerted on the particulate matter are low which diminishes the efficiency of particulate removal. The low energy cohesive density of liquid CO<sub>2</sub> hinders the dissolution of surfactants. Thus, the number of surfactants that are CO<sub>2</sub>-philic is limited [139]. CO<sub>2</sub>-philic surfactants are amphiphilic compounds that contain CO<sub>2</sub>-philic and phobic parts. Generally, the tails have an affinity for CO<sub>2</sub> and the head group is phobic (Figure 5-8). Also, CO<sub>2</sub> acts as Lewis acid which makes it an electron-accepting liquid. This property helps CO<sub>2</sub> in participating in acid-base interactions with various substrates. The primary requirement for the CO<sub>2</sub>-philic surfactant is to have strong interaction with CO<sub>2</sub> molecules and minimum intermolecular interactions. Thus, having branched tails, low-molecular-weight hydrophobic tails, methyl groups help in fulfilling the above requirement [146].



*Figure 5-8: General structure of CO<sub>2</sub>-philic surfactant.[146]*

In an experiment, about 130 commercial surfactants have been tested in liquid CO<sub>2</sub> and none of them showed promising results [145]. The primary reason is overcoming surfactant tail-tail attraction in liquid CO<sub>2</sub>. Modification of detergents to increase the solubility included replacing hydrogen with fluorine in the apolar tail of the surfactant since fluorine and CO<sub>2</sub> have similar cohesive energy densities. This modification was not entirely successful since it included increasing the pressure above 150 bar to solubilize these surfactants along with fluorine itself being an environmentally toxic chemical [145] [147] [148]. The second modification included introducing a hydrocarbon branching in the non-polar tail since branching creates low-density structures that dissolve easily in liquid CO<sub>2</sub>. The result indicated that the surfactant had a cloud point at higher pressure, but it was still soluble at pressure larger than the pressure applied in dry cleaning [149]. Banerjee in his study of surfactant formulation for particle release in non-polar medium stated the required properties of a surfactant in liquid CO<sub>2</sub> that were: (1) strong

adsorption or wetting by the surfactant at the fabric-soil interface, (2) increasing the viscosity of liquid CO<sub>2</sub>, (3) including water as a cosolvent to remove polar soils, and (4) including n-alkanes to improve solvency power of liquid CO<sub>2</sub>. Also using n-heptane a short-chained alkane of 30 % (v/v) improved the solvency of liquid CO<sub>2</sub> [150].

CO<sub>2</sub>-philic surfactants are also used in EOR applications which incorporate the non-polar nature of CO<sub>2</sub> simultaneously decreasing its mobility which is an ideal condition for EOR. Branching, adding more tails to the surfactants, introducing carbonyl group are the modifications at increasing CO<sub>2</sub> affinity to the surfactants [151]. Various research has been conducted over the years to improve CO<sub>2</sub>-water emulsion stabilization. Hydrocarbons have been used since they are economical, environmentally benign but exhibit low CO<sub>2</sub>-philicity. Surfactants such as poly (ethylene oxide)-b-poly (butylene oxide) emulsified up to 70% CO<sub>2</sub> with droplets of 2-4 μm in diameter but the emulsion has limited solvation due to CO<sub>2</sub>. Also, the pressure required to keep emulsion stabilized is higher [152]. Several polyvinyl acetate-based hydrocarbons have demonstrated good CO<sub>2</sub>-philicity. The addition of copolymers such as dibutyl maleate weakens polymer-polymer interactions that improved CO<sub>2</sub>-philicity [153]. A branched non-ionic surfactant study concluded that the surfactant along with n-hexane as cosolvent improved soil removing ability. The surfactant, when used as pre-treatment, showed five times better results than the control liquid CO<sub>2</sub> [145]

Thus, improving the physical properties of liquid CO<sub>2</sub> by introducing a surfactant will help in improving the detergency of liquid CO<sub>2</sub> and will improve the prospects of cleaning using liquid CO<sub>2</sub>.

## 5.7 *Pressurized CO<sub>2</sub> applications*

Supercritical CO<sub>2</sub> has been investigated as an effective solvent for the last two decades. Considering its efficiency, customized solvent strength, and gas-like properties, sc-CO<sub>2</sub> is an ideal alternative for conventional solvents for extraction. The sc-CO<sub>2</sub> has been widely used in the cleaning industry. Non-toxicity, readily available makes supercritical CO<sub>2</sub> almost a versatile solvent. Apart from textile industry CO<sub>2</sub> has been used in pharmaceuticals [154] [155], improving polymer processing [156] [157], extraction of natural oils such as jojoba, CBD [138] [158], dyeing industry [159] [160] [161] [162]. The sc-CO<sub>2</sub> has been commonly used in oil recovery, processing of petroleum products. It has been regularly used as a miscible flooding agent for enhanced oil recovery. Primary and secondary oil recovery contributes only (15-30) % of the original oil in the reservoir whereas sc-CO<sub>2</sub> can help in accelerating the recovery of heavy hydrocarbons. The recovery of hydrocarbons in pressurized CO<sub>2</sub> demonstrated the mobility of non-polar hydrocarbons in the medium. This property of pressurized CO<sub>2</sub> to extract non-polar compounds can help in removing the shortcomings of polar aqueous medium where hydrocarbons do not partition so easily.

Products from natural sources contain biological or biochemical contaminants such as bacteria, viruses, spores. Eliminating such toxic contaminants are very important in the pharmaceutical and food industry. The sc-CO<sub>2</sub> can be used in low-temperature sterilization for such products [133]. Low-temperature sterilization can be an effective technique in decontaminating PPE from blood pathogens, bacteria, etc.

### 5.7.1 *Cleaning*

Dry cleaning is a process of removal of soil/from a textile substrate using a non-aqueous solvent since these materials can shrink/wrinkle due to water. Perchloroethylene (PERC) is

commonly used as a dry-cleaning solvent in the textile industry. The drawbacks of using PERC are several of which the prominent are harmful to the environment, probably carcinogenic. CO<sub>2</sub> has replaced PERC due to its non-toxicity, better solvent properties, environment friendly. In dry cleaning applications, liquid CO<sub>2</sub> is preferred over scCO<sub>2</sub>. For washing, the pressure and temperature parameters are adjusted in such a way that system is always at the two-phase boundary line. The liquid CO<sub>2</sub> applications in dry cleaning have been very less explored [133]. Several studies have concluded that the results for non-particulate soil removal that includes fats, proteins are better for liquid CO<sub>2</sub> cleaning than PERC. For particulate matter such as clay, sand, etc PERC is more efficient than liquid CO<sub>2</sub> [139]. Introducing mechanical action can have a huge impact on cleaning particulate matter. Acoustic cavitation is one of the techniques which is used in cleaning technologies to induce a mechanical action. Ultrasound generates transient bubble formation that generates fluid jets and shock waves which are used for cleaning. Ultrasound is a pressure wave created by a frequency above 16kHz. For cleaning purposes, the frequency range used is 20kHz-120kHz. Both negative and positive pressures are important in producing cavitation since the former is responsible for bubble formation while the latter implodes the bubbles which produce the shock-wave used in cleaning [163].

Redeposition of particulate soil is one of the major problems in dry cleaning and happens due to insufficient stabilization which leads to graying of the fabric. Thus, it will be interesting to evaluate the performance of liquid CO<sub>2</sub> on the legacy gears since the contaminants are in particulate form. In an aqueous medium, redeposition can be resolved by adding anti-redeposition agents in a detergent formulation such as sodium carboxymethyl cellulose, polymeric cellulose acetate, polyvinyl alcohol. Anti-redeposition agents stabilize the charges by increasing the electrostatic repulsion between soil particles. For CO<sub>2</sub> medium no commercially

available solutions are available although several patents have been registered giving different suggestions such as:

- Adding a rinsing step with compressed purge nitrogen gas after the cleaning step. Purged gas will interpose between the substrate and removed soil to avoid redeposition.
- Eliminating the static charge by incorporating ionized gas.
- The high flow rate of 1 gallon per pound of fabric for recycling of CO<sub>2</sub> stream and passing it through a series of filter papers to decrease the possibility of redeposition.
- Adding cellulose-based anti-redeposition agents helped redeposition in CO<sub>2</sub> medium by 87% and is highest among all the methods described [144]
- Using a co-solvent such as n-hexane improved the cleaning efficiency while cleaning lubricating oil waste from plastics [164]. Supercritical CO<sub>2</sub> has replaced sulfuric acid/hydrogen peroxide mixtures in cleaning microelectronics. Its excellent solvent properties are much more efficient in cleaning delicate parts, complex assemblies for organic contamination removal [138].

From all the above discussion it can be concluded that high-pressure CO<sub>2</sub> has several advantages over the conventional dry-cleaning methods. Although it has several limitations regarding low efficiency against polar contamination, low-mechanical action in removing solid particles can be overcome using polar co-solvents, acoustic cavitation, etc. Extraction of organic compounds in liquid CO<sub>2</sub> or sc-CO<sub>2</sub> provides high yield and recovery of CO<sub>2</sub> by depressurizing after use makes it an economical, environmentally-friendly solvent.

Most of the fireground contaminants that we are investigating are non-polar thus confirming their high removal from the turnout suits. Thus, with its distinct physio-chemical properties and

versatility in applications sc-CO<sub>2</sub> can be used in our quest for the decontamination of firefighters' PPE.



## Chapter 6: Gas Chromatography

Gas chromatography (GC) (Figure 6-1) is an analytical technique used for qualitative and quantitative analysis of organic compounds. GC uses a gaseous mobile phase to carry the sample analytes through a stationary phase which is a column comprising different polymers. The GC can analyze solids, liquids, and gases that have a molecular weight in between 2 to 800 molecular atomic units, and the typical operating range is 10-400°C. The GC technique uses the difference in the boiling points of various compounds and their chemistry with the stationary phase to separate them from the mixture. This technique is used in a variety of applications such as cosmetics, pharmaceuticals, petrochemical, etc [165]-[167]

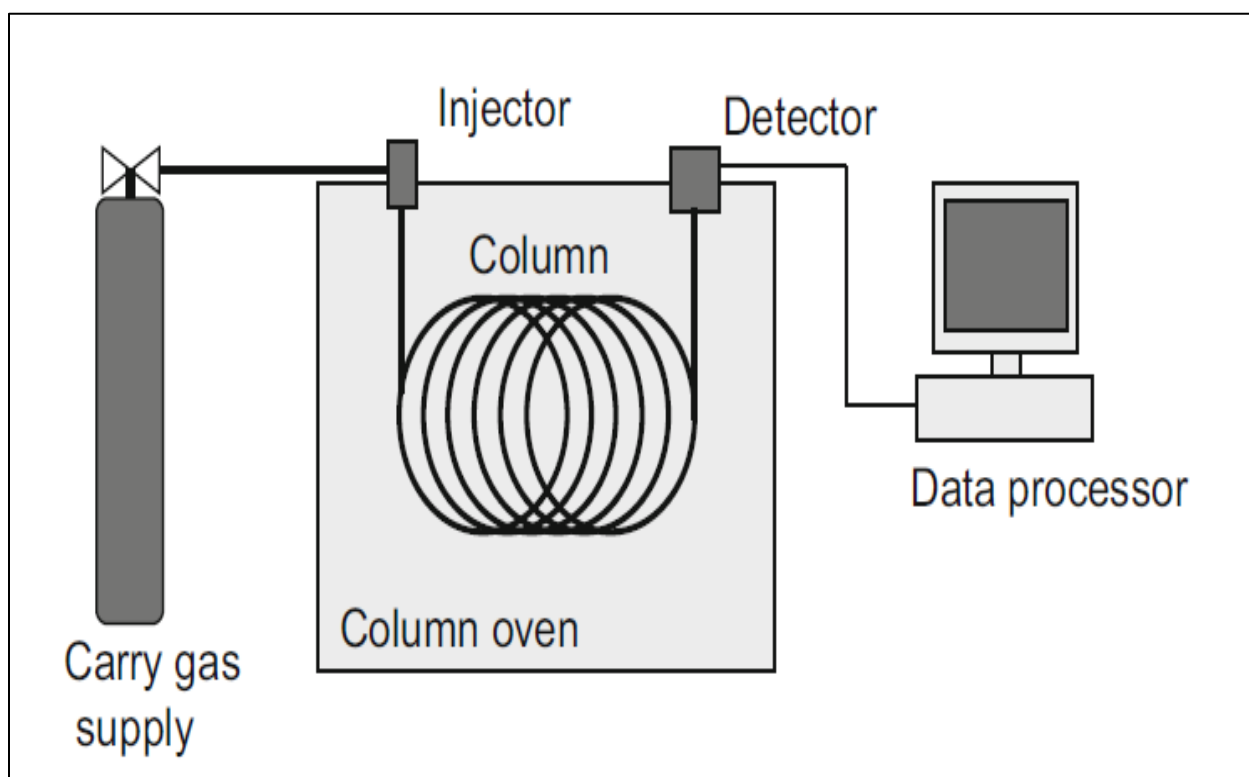


Figure 6-1: Gas-Chromatography instrument. [167]

### 6.1 Mass spectrometry

Mass spectrometry (MS) is an analytical-instrumental method used in association with other analytical techniques such as GC to determine the structure of the compounds (Figure 6-2).

The MS technique consists of bombarding vaporized organic molecules in a vacuum with high-energy electrons and measuring the mass-to-charge ( $m/z$ ) ratio. Thus, it is the identification of the compounds based on the atomic composition of the molecules and their charged state. The output of GC-MS is a mass spectrum which is a plot of mass-to-charge ratio [168], [169].

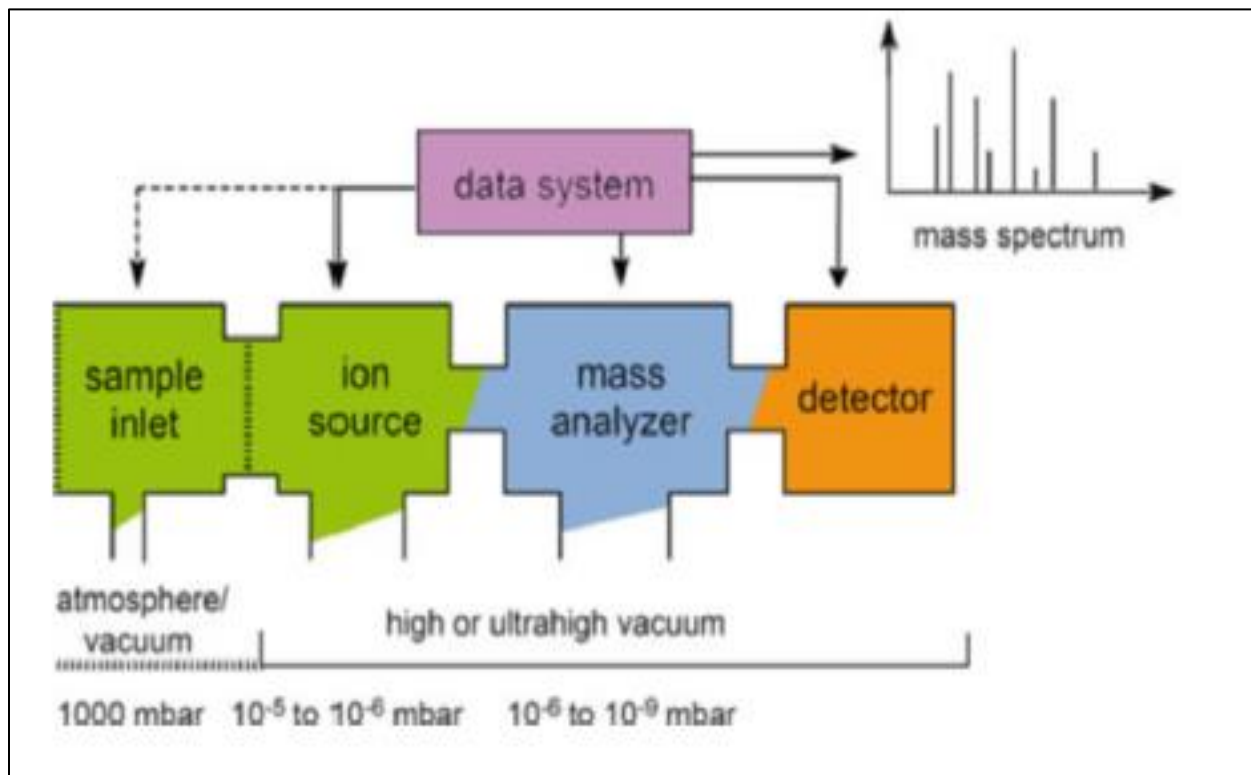


Figure 6-2: Schematic of mass spectrometer.[170]

## 6.2 Flame Ionization Detector (FID)

FID (Figure 6-3) is a widely used detector and is used with GC-specific applications. Due to its high sensitivity and linear range for carbon-containing compounds, it is very popular in organic analysis. The effluent is mixed with hydrogen gas before exiting through a small orifice that is surrounded by a high flow of air. The stoichiometry of hydrogen gas, effluent, and the air is important. The burning of an effluent produces ions that form a small current when a potential difference is applied. The jet forms the anode and a cylindrical electrode held above the flame is the cathode. A voltage of 200-300V in between these components is optimal. The FID response

is proportional to the number of carbon atoms in a molecule. The suggested reason for this is the conversion of all solute carbon molecules to methane. With the presence of heteroatoms, the sensitivity of the FID is reduced [171].

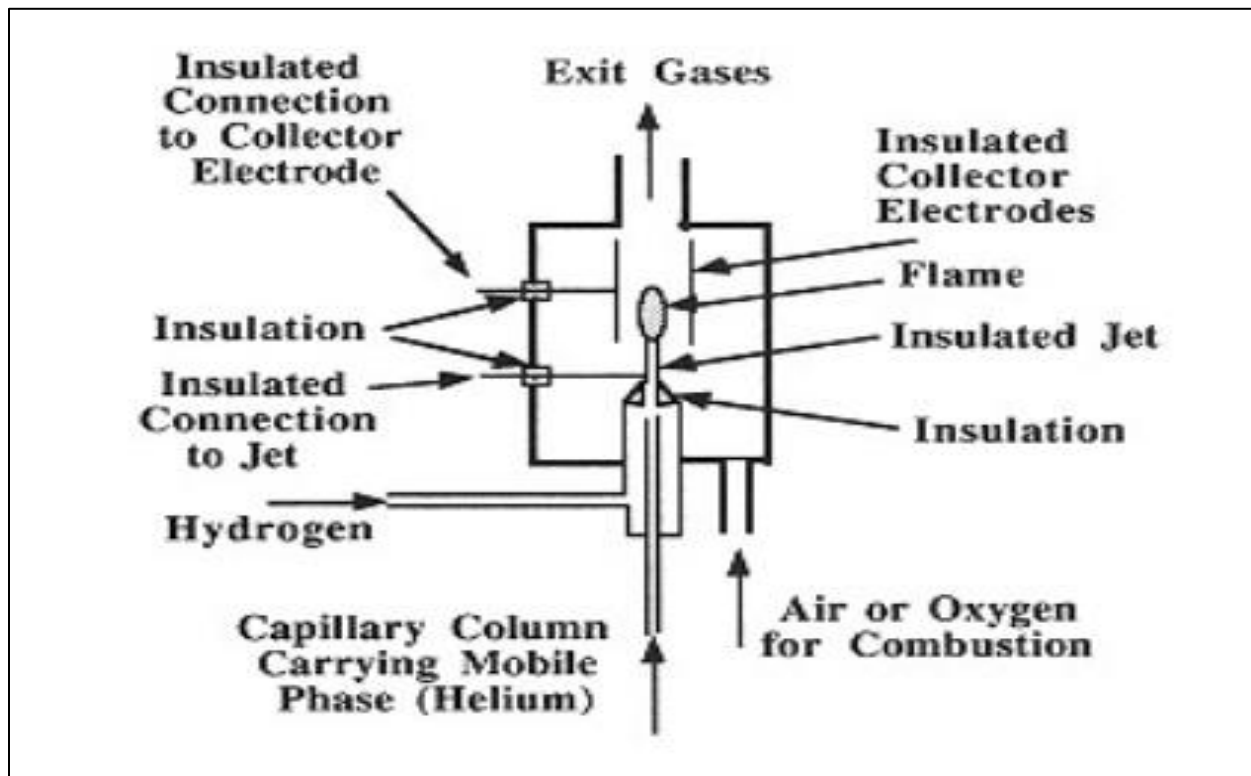


Figure 6-3: Schematic of FID.[172]

### 6.3 Previous studies on analysis using GC

#### 6.3.1 Phenols

Several studies have been devoted to the identification of organic contaminants such as phenols in municipal waters, various flavored drinks, drinking water, etc. Phenols and their substituents comprise both volatile and semi-volatile compounds making them suitable for analysis using GC instruments. In a study conducted by EPA, the phenols were identified using Method 604. The sample (approximately 1L) from sewage was acidified and extracted with methylene chloride using a separatory funnel. The extract was dried and mixed with 2-propanol to a volume of 10mL or less. The GC-FID was used to analyze the compounds. The column used

was a 1.8 m long X 2mm ID glass, packed with 1%SP-1240 DA on Supelcoport (80/100 mesh) [173].

Mass spectrometry technique has also been used in identifying phenols from sewage samples. At low concentrations, the sensitivity of the chromatographic instruments (GC or HPLC) along with MS is not enough. The pre-treatment of a sample, such as liquid-liquid extraction with organic solvents such as n-hexane, dichloromethane is used due to their polar nature to improve the sensitivity. Columns such as C8, C18, DB-5MS fused silica (phenylmethyl siloxane) are also used in the analysis of phenols [174]-[176].

Derivatization is a technique used when the incompatibility issues such as mismatch polarity, and/or volatility occur. A derivatizing agent such as N-methyl-N-tert-(tert-butyl)dimethylsilyl) trifluoroacetamide is commonly used [176]. The operating temperatures have been noted from 40 °C to 280 °C for most of the studies and a slow increase in the temperature produces better resolution [172]-[176].

### 6.3.2 *Phthalates*

GC is the widely accepted analytical technique in the determination of phthalates. The capillary columns coated with non-polar stationary phases (poly-dimethyl-siloxane or poly-methyl phenyl-siloxane) are used in GC separations as they provide better resolution, higher operating temperatures and low bleeding as compared to the columns coated with polar stationary phases (polyethylene glycol, wax, cyanopropyl). Long columns and slow temperature ramp rate programs can provide better resolutions. Solvents such as dichloromethane, hexane, acetone have been used in detecting phthalates in GC [75].

The MS is the best method for detecting phthalates since they are robust, economical, and provide linear range [177]. Several studies have used the GC-MS technique to analyze phthalates

in pharmaceuticals [177], food matrices [75], wine [178], bottled water [179]. An EPA study was performed to analyze the contamination in gloves and hoods used by firefighters. The samples were analyzed using methylene chloride and the method used was EPA 8270D. Results indicated the presence of phthalates in the samples confirming the contamination [180].

### 6.3.3 PAHs

PAHs are frequently measured in the atmosphere to perform quality assessment of air, sediments for environmental monitoring, biological tissues for health monitoring, etc. GC and liquid chromatography (LC) both are used prominently in the analysis of PAHs by EPA [181]. The EPA has analyzed PAHs for all types of samples regardless of water content that including soils, sediments, wastewater, etc [182]. The EPA Method 610 is used in analyzing 16 PAHs and describes both GC and LC methods unlike the EPA Method 625 that describes only the GC-MS method. Many studies have used LC-GC coupled methods to examine a wide range of analytes and to have double confirmations for the determination of compounds. Many federal agencies such as the National Institute for Occupational Safety and Hazard, the Association of Analytical Chemists, American Public Health Association used LC and GC for analysis of PAHs[ [181].

The length of the columns for environmental applications ranges from 15m-60m and the diameter ranges from 0.25mm-0.32mm. Methyl and phenyl substituted polysiloxanes are widely used in columns. The development of stationary phases for GC is continuing. Cold on-column injections are preferred since they give better resolutions. For environmental applications, capillary columns with GC-MS are preferred over LC-MS since the former offer greater selection, resolution and selectivity than the latter one [181].

Briefly explained, from the EPA and other standard methods, the selection of GC-MS would be better when analysis of firefighter turnout samples needs to be done. The analysis of

fireground contaminants is very similar to the analysis performed using EPA methods. From the previous decontamination studies, the key highlight was there is a high variation in the contamination both qualitatively and quantitatively. The proper choice of a column, the solvent would be very important to obtain better resolution and selectivity of the various fireground contaminants.

## Chapter 7:Extraction

A variety of extraction techniques have been used in the analytical chemistry field. Extracting different organic, inorganic compounds from various mixtures is a complicated process that is based on a variety of factors like temperature, pressure, solvent-solute chemistry, etc. Traditional methods include Soxhlet extraction, maceration, percolation, and sonication which can be placed into the category of solid-liquid extraction. These conventional techniques are very time-consuming and consume high volumes of solvents which may or may not be environmentally friendly. Modern techniques include microwave-assisted extraction, pressurized solvent extraction, supercritical fluid extraction which are efficient and much quicker than the conventional ones [183].

### 7.1 *Pressurized Solvent Extraction*

#### 7.1.1 *Instrumentation and Theory*

Dionex Corporation in 1995 launched an accelerated solvent extraction system that established the premises for pressurized solvent extraction. Figure 7-1 illustrates the schematic of the pressurized solvent extraction system. The sample (solid or semi-solid) is placed in the steel extraction cell which is filled with solvent or a solvent mixture, and the cell is heated at high temperatures under pressure. In a single extraction cycle, when the solvent is heated it expands thus increasing the pressure of the cell. The pressure range in the cell is around 35-200 bar and the temperature range is about 30°C -200°C. A static valve opens if the pressure in the system exceeds the setpoint and closes automatically. After holding up the solvent in the cell at high temperature and pressure for around 5 mins, the solvent is flushed out and collected into the collection vials. Collection vials have a volume of 20 mL, 40 mL, and 60 mL. The tubing in the system is chemical resistant and contains a needle at the end which punctures the septum in the

lid of the collection cell. After this static extraction stage, the system is flushed out with fresh solvent pumped into the system which flushes out cells and tubing. Nitrogen gas is compressed and used to purge out the solvent present in the system. A single extraction experiment can comprise multiple cycles which cumulatively increases the extraction of the analytes [184].

The principle of pressurized solvent extraction is that organic solvents at high temperatures and pressure are used to extract compounds from matrices [184]. Increased temperature accelerates the chemical kinetics of the extraction and high pressure maintains the liquid state of the solvent. Also, the elevated pressure forces improve the penetration of the solvent facilitating the extraction of the analytes [183]. The two steps that need to be considered in PFE:

#### *7.1.2 Mass Transfer and solubility*

High pressure and temperatures enhance the diffusivity of the solvent improving the extraction time of the solvent. Adding a fresh solvent during the operation increases the concentration gradient between the solvent and surface matrix which leads to an increase in the extraction rate. The ability of the solvent to solubilize contaminants increases with an increase in temperature. Considering Figure 7-2 it can be concluded that glycine solubility increases with increasing temperature. Higher pressure in an extraction cell keeps the solvent liquefied above their boiling points thus promoting solubility effects. At higher temperatures, diffusion rates are higher which leads to improved mass transfer rates [184].



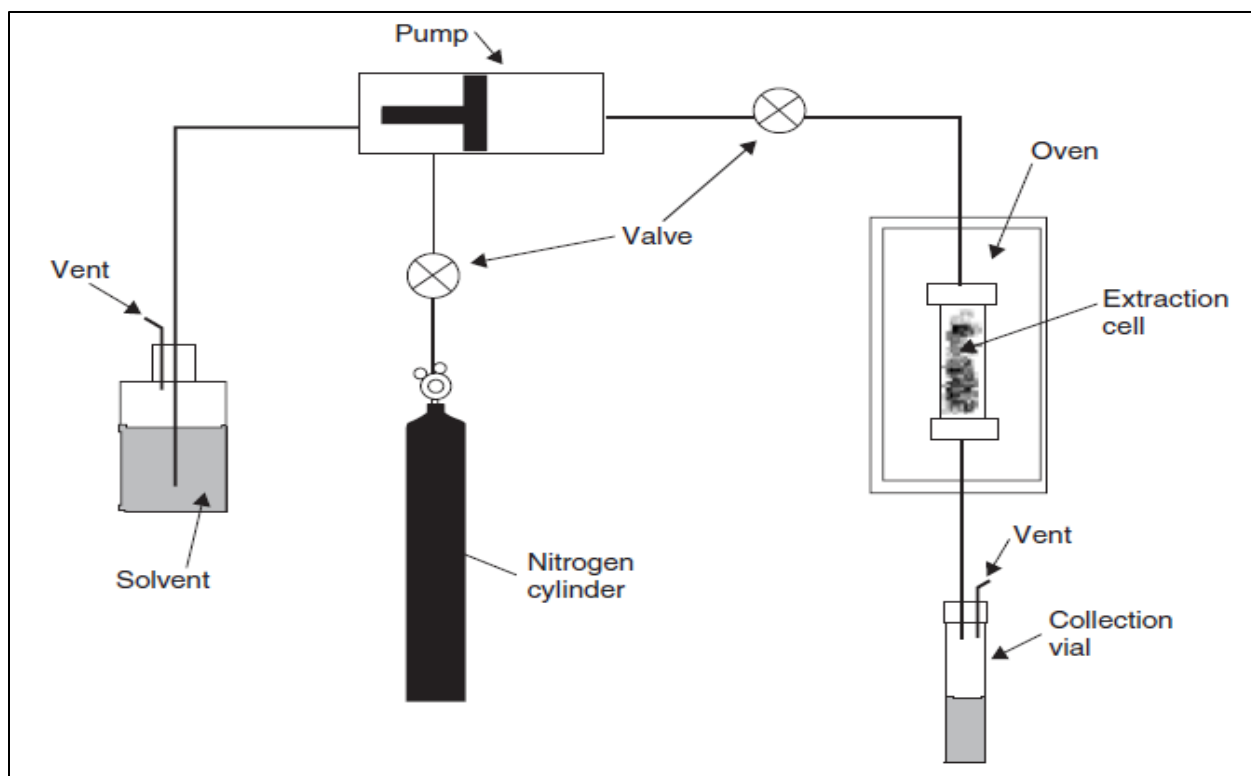


Figure 7-1: Schematic of the pressurized solvent extraction system.[184]

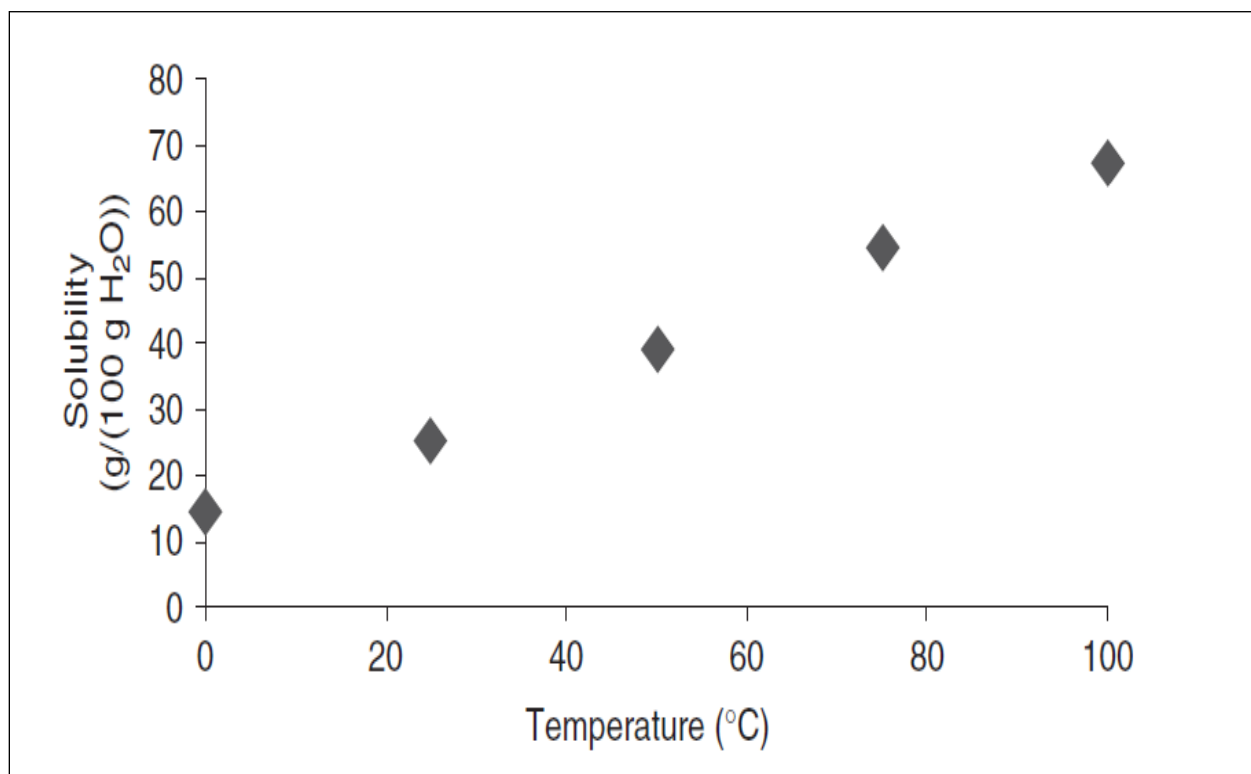


Figure 7-2: Influence of temperature on glycine.[184]

### 7.1.3 Surface equilibria disruption

The temperature and pressure combination has symbiotic benefits. This improves the recovery of organic compounds from sample matrices. As the temperature increases within the extraction cell, it disrupts the analyte-matrix interactions (hydrogen bonding, van der Waals forces, dipole interactions). The viscosity (Figure 7-3) and surface tension (Figure 7-4) of the solvent decrease with rising temperature thus improving the penetration of the solvent within the matrix increasing the extraction efficiency [184].

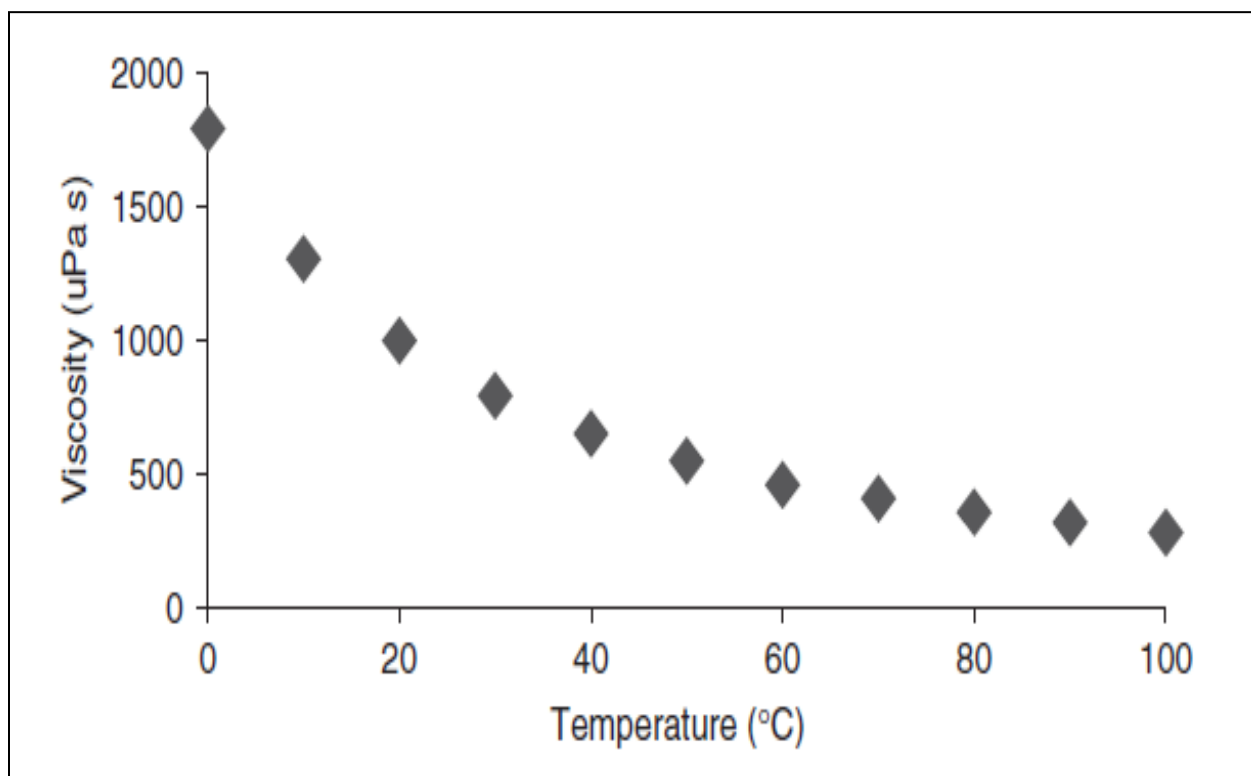


Figure 7-3: Influence of temperature on viscosity of water. [184]

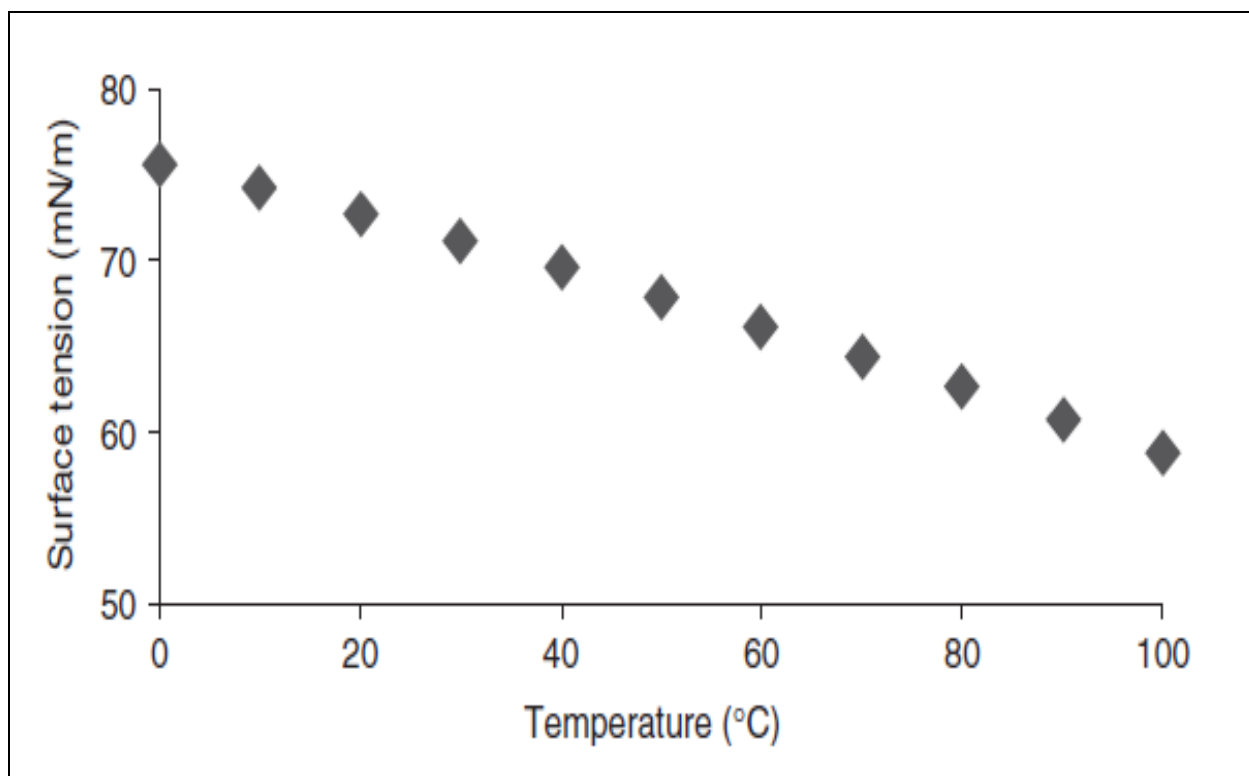


Figure 7-4: Influence of temperature on the surface tension of water. [184]

#### 7.1.4 Sampling considerations

Sampling strategies play a vital role in the analysis of samples. There are two types of sampling: random and purposeful. The sampling process involves the selection of sample points, size of the sample area, the shape of a sample area, number of sampling units. Random sampling as the name suggests involves no selectivity. Types of sampling in terms of matrices: soil and sedimentation, air sampling, water sampling [184].

#### 7.1.5 Method development

Incorporating certified reference materials helps in assessing the analysis and extraction process and sets up a benchmark for the procedure. This improves the precision and accuracy of the procedure.

#### *7.1.5.1 Pre-extraction*

The first step is the identification of organic compounds that needs to be recovered. This includes assessing solubility parameters, physical properties which help in selecting extraction solvents. The sampling matrix is either a wet or moisture-laden surface that encounters the solvent. The sample size is a very important parameter as the smaller the sample particle size, the greater the interaction with the extraction solvent. Packing of the cell is very important as dead or void volume can disrupt the extractions efficiencies [184].

#### *7.1.5.2 Extractions conditions*

It is necessary to use high-purity solvents to minimize chromatographic errors. The choice of solvent is considered according to the nature of compounds (polar/non-polar). Operating parameters such as extraction time (static and dynamic), temperature, pressure need to be optimized. The majority of the compounds are extracted after an extraction time of five+five minutes. The temperature of the process has a huge benefit from 50°C up to 150°C. However, a higher temperature can degrade organic compounds and solvents hence it needs to be optimized. The pressure of around 2000 psi is appropriate for the extraction of solvents [184].

#### *7.1.6 Applications*

PFE has been in vogue in recent years over conventional extraction techniques. PFE has several advantages such as brief processing time, less consumption of solvents, higher extraction efficiencies that make it a popular choice over conventional methods. The inclusion of PFE in the EPA method for determining persistent organic pollutants in environmental samples accelerated its use in analytical chemistry [185]. PFE has been successfully used in the extraction of PAHs [186], phthalates [187]. Thus, incorporating PFE in the extraction of the

fireground contaminants from the PPE could provide a fast, reliable method for qualitative and quantitative analysis.

## **Chapter 8:Development of the Bench-Scale Washing Method**

*The following chapter includes excerpts from the research article submitted for review*

### **8.1 Introduction**

The materials found in modern buildings and furnishings are synthetic that can generate several toxic combustion byproducts. Firefighters are exposed to such chemicals during the suppression of fire. As seen from Section 2.3, various studies have indicated that phthalates, phenols, and PAHs are frequently found on PPE. Traditionally, laundering of PPE following every fire suppression response was not a universal practice; however, it has become an encouraged and accepted protocol in recent years. Due to irregular cleaning, toxic substances can accumulate on the gear from each consecutive fire response, and the dermal exposure to these substances may be harmful to the firefighters [12]. Field decontamination, gross decontamination, or preliminary exposure reduction has been recently added in the practice and performing it following a fire response may remove many such contaminants. The NFPA 1851 (2020 edition) standard on selection, care, and maintenance has added field decontamination and routine cleaning in Chapter 8 [188]. The NFPA 1851 standard has prescribed guidelines for decontamination. For the advanced cleaning, guidelines have clearly stated a minimum of two advanced cleanings in twelve months [188]. The advanced cleaning consists of using a programmable washer/extractor followed by all gear being air-dried with good ventilation.

Some of the studies discussed in Subsection 2.3 used various techniques to assess the decontamination efficiency but a controlled study for measuring the cleaning efficiency of the washing method according to the NFPA 1851 method is not available. Subsection 12.6 in this standard has stated test procedures for evaluating semi-volatile organic compounds. The test procedures describe steps for preparation, extraction, and analysis. The method describes

washing of the contaminated swatches on the full-scale washer-extractor using surrogate garments. A washing procedure can have multiple variables including the temperature of the bath, duration of the washing cycle, rinsing cycles, detergent used in washing, the concentration of the detergent, among others. Establishing a standard procedure on a bench-scale will help in instituting a uniform practice to determine the cleaning efficiency of various cleaning products available in the market. The equation described in NFPA 1851 in Subsection 12.6.5.4 calculates the cleaning efficiency for each contaminant (Equation 8-1).

$\text{Cleaning efficiency} = \left(1 - \left[\frac{(C_c - C_m) - (C_w - C_p)}{(C_c - C_m)}\right]\right) * 100$	<p style="text-align: right;">Equation 8-1: Cleaning Efficiency (NFPA 1851)</p>
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where,

$C_c$  = contaminated specimen (unwashed, contaminated)

$C_m$  = material specimen (unwashed, not contaminated)

$C_w$  = contaminated specimen (washed, contaminated)

$C_p$  = material specimen (washed, not contaminated)

Since it is stated to consider the value of mass below the detection limit as 0, the use of  $C_m$  and  $C_p$  terms gets nullified as they both are negative controls or background measurements for the experiment. The standard practice is to report a value of one-half the limit of quantitation (LOQ) if the contaminant is not detected in the calibrated range. This approach accounts for the instrument sensitivity and indicates that the contaminant can be present at trace amounts that are beyond the limits of the instrument and analytical method. This analytical principle is not rationalized in the NFPA 1851 standard. Cleaning efficiency can be calculated by a direct comparison of the  $C_c$  and  $C_w$  values. A negative control when extracted and analyzed should be

considered in the equation only if the value is present. Thus, the modified equation to calculate Cleaning Efficiency (%) looks like this:

Cleaning efficiency (%) =	<i>Equation 8-2: Cleaning Efficiency</i>
$\frac{(\text{Original concentration}(C_c) - \text{post washing concentration}(C_w))}{\text{Original concentration}} * 100$	

Where  $C_c$  is the original concentration present and  $C_w$  is the concentration of the contaminant present on the fabric after washing. The cleaning efficiency is the amount of the contaminant removed from washing. A specified number of replicates will help in assessing the variability of the experiments and will help in inferencing the significance of the effect of the factors involved in the study. Thus, a standard washing procedure is required for the assessment of the specimens. A bench-scale washing procedure can be used as a standard test in evaluating cleaning efficiency. Bench-scale washing has several advantages including being economical, efficient, and all the parameters can be controlled.

Over the years, bench-scale washing protocols have been implemented for comparison of surfactants and washing techniques in assessments of removal of PAHs [189], [190]. Thus, implementing bench-scale washing in evaluating current washing procedures for firefighter gear is justified.

The following study details the development of a bench-scale protocol for firefighter turnout materials contaminated with known concentrations of targeted fireground contaminants and washed in a controlled environment using commercial surfactants. The primary aim of the study was to test the consistency of the bench-scale washing method so that it can be used in further research.



## 8.2 Materials and Methods

A custom calibration standard (referred to as ‘master mix’) of three phenols, three phthalates, and three (PAHs) prepared in methylene chloride was purchased from Agilent Technologies. The mix had all compounds at a concentration of 2,000 ng/μL and was packaged in 2-mL amber vials and stored in the refrigerator at 4°C. The compounds in the master mix and selected properties are provided in Table 8-1.

Table 8-1: Targeted Contaminants in the mix.

<b>Compound</b>	<b>Boiling Point (°C)</b>	<b>Volatile/ Semi-volatile</b>	<b>IARC<sup>a</sup> Classification</b>	<b>K<sub>ow</sub></b>
<b>Phenol</b>	182	Volatile	Group 3	1.46
<b>2,4,6- Trichlorophenol (2,4,6-TCP)</b>	246	Volatile	Group 2B	3.69
<b>Pentachlorophenol (PCP)</b>	310	Semi-volatile	Group 2B	5.12
<b>Di-butyl phthalate (DBP)</b>	340	Semi-volatile	Group 3	4.50
<b>Benzyl butyl phthalate (BBP)</b>	370	Semi-volatile	Group 3	4.73
<b>Di-ethylhexyl phthalate (DEHP)</b>	384	Semi-volatile	Group 2B	7.60
<b>Phenanthrene</b>	340	Semi-volatile	Group 2B	4.46
<b>Pyrene</b>	404	Semi-volatile	Group 3	4.88
<b>Benzo[a] pyrene (BaP)</b>	495	Semi-volatile	Group 1	6.13

### 8.2.1 Gas Chromatography/Mass spectrometry

The analysis of the fireground contaminants was carried out using an Agilent 7890B Gas Chromatographic (GC) system coupled to an Agilent 5977B Mass Spectrometer (MS) equipped with Electron Ionization (EI) capability. Chromatographic analysis was conducted in the splitless mode with a purge flow of 100 mL/min at 1.0 min. The Agilent Ultra Inert liner (5190-6168, straight 2 mm ID) was used in the GC inlet which was maintained at 250°C. An Agilent EPA 8270D fused silica capillary column (30 m × 0.25 mm × 0.25 μm) was used with a helium flow rate of 1.2 mL/min. The oven program was set to begin at 40°C, then increased to 280°C at a rate of 10°C/min with a 1-minute hold, followed by a further increased to 300°C at 25°C/min with a final hold of 1 minute. The total running time was 30.48 min. The MS transfer line was kept at 280°C throughout the run. The MS quad temp was maintained at 300°C and the ion source temp was kept at 200°C. The gain factor used was 1.00. The analysis was conducted in scan mode (35-550 amu) using EI with an energy of 70 eV.

### 8.2.2 Calibration Curve for the compounds

The instrument was calibrated using the master mix of compounds (2,000 ng/μL for each compound) as the stock solution. The calibration standards given in the Table 8-2 were made from the stock and diluted to volume with n-hexane (Fisher Scientific-95 % purity) in a 10-mL volumetric flask. The calibration curve was obtained by averaging out the responses of three replicates. For a limit of detection (LOD) and LOQ values the low standard (0.6 ng/μL) was run 7 times to calculate the standard deviation (σ) of the area. The LOD and LOQ is calculated using the formula given by Equation 8-3 & Equation 8-4 [191].

$$\text{LOD} = 3\sigma/m$$

*Equation 8-3: LOD*

$$LOQ = 10\sigma/m$$

Equation 8-4: LOQ

Table 8-2: Calibration solutions for the chromatography method.

Calibration Standard	Target Concentration (ng/μL)	The volume injected from the stock solution (μL)	Mass per unit area (ng/cm <sup>2</sup> )
1	0.6	3	240
2	1.2	6	480
3	3	15	1200
4	6	18	2400
5	9	45	3600
6	12	60	4800

### 8.2.3 Extraction

All fabric samples were extracted using the Buchi Speed Extractor E-916 with n-hexane (Fisher Scientific) as the extraction solvent. Each extraction was comprised of two full extraction cycles and one flush cycle at the end. Every single extraction cycle consisted of a five-minute heat-up followed by a five-minute hold where the solvent and fabric were in contact with each other. The cycle was held at 100 °C and 100 bar, and the extraction was carried out in the nitrogen atmosphere since it was inert. Outer shell fabrics (pre-wash or post-wash) of size 5 cm X 5cm were placed in the 10-mL stainless steel extraction cell. Glass beads were sonicated with n-hexane to remove any prior contamination, and 5 grams of glass beads were filled inside each cell to fill the void volume to reduce the excess solvent entering the cell. The cell was capped with top and bottom cellulose filters to prohibit unwanted particulate contamination. The extract passed through a condensing coil and was collected in a 60-mL glass vial. The total run time for the extraction process was 32 minutes.

After collecting the extract from each cycle, it was diluted to 10 mL in a standard 10-mL volumetric flask using n-hexane. A sample of the diluted extract was filtered out into the 2-mL amber autosampler vial using a 3-mL Luer-lock syringe with 0.2 µm PTFE filters. These vials were loaded on to GC-MS system and analyzed.

#### *8.2.3.1 Extraction Efficiency*

The extraction efficiencies for each compound were determined using three outer shell fabric swatches (5cm x 5 cm) spiked with the master mix of contaminants to achieve 100000 ng of each contaminant on the swatch. A positive control consisted of directly spiking the liquid into the extraction cell with no fabric, and a negative control consisted of an uncontaminated fabric swatch. The concentration obtained from the positive control was the maximum extraction efficiency achieved through the cycle hence was considered as 100%. The concentration obtained through the contaminated fabric was then used to calculate the relative extraction efficiency. This helped in understanding how well the fabric holds the contaminants.

#### *8.2.4 Testing variation in bench-scale washing method*

The bench-scale washing was performed using the LSE Corning bench-top shaking incubator (Figure 8-1). The primary aim of the portion of the study was to test the consistency of the bench-scale washing method. Thus, two commercial detergents (CD) (CD-1 and CD-2) were used to wash three contaminated fabric samples each on three different days (Table 8-3). Thus, six samples a day and in total 18 samples. The CD-1 is a popular detergent in the firefighting community, and CD-2 is a common home laundry detergent.

Table 8-3: Experimental design for testing consistency.

Day 1		Day 2		Day 3	
CD-1	CD-2	CD-1	CD-2	CD-1	CD-2
Sample-1	Sample-1	Sample-4	Sample-4	Sample-7	Sample-7
Sample-2	Sample-2	Sample-5	Sample-5	Sample-8	Sample-8
Sample-3	Sample-3	Sample-6	Sample-6	Sample-9	Sample-9

The controlled contamination was performed using a repeater pipette (Eppendorf) to dispense a total of 100,000 ng of each contaminant on the fabric swatches (5 cm x 5 cm). The swatches were made from PBI Max™ Gold (7 oz.), a common outer shell fabric that also has a durable water-repellant finish.

The fabric swatches ( $0.7 \pm 0.03$  g) were placed into 250-mL Erlenmeyer flasks and 4.3 grams of glass beads were added to each flask to provide mechanical agitation. The total weight of the material (fabric) was 0.7 grams. The liquor ratio was kept at 142:1; hence the total volume of the water used for the washing was 100 mL. Such a high ratio was used since the fabric needed enough water to be completely immersed in the solution. The contents of the flask are shown in Figure 8-2.

The MSDS recommended amount for a commercial detergent is 6 oz for a 45 lbs. load. For bench-scale washing, the amount of detergent was scaled down. The weight of the load was 5 grams. The weight of one single swatch is 0.7 grams and we used 4.3 grams of the glass beads to make the total weight of 5gms. Thus, by proportionating the 6 oz with 45 lbs. we calculated the amount of detergent to be added was 45  $\mu$ L. All the samples were washed at 40°C for 60 minutes. The liquid from the flask was drained and 100 mL of clean water was added to rinse the samples for 10 minutes at room temperature. Post rinsing, the samples were air-dried for 24

hours. The next day the samples were extracted with a pressurized solvent extractor and subsequently analyzed following the described GC-MS method. The process is shown in Figure 8-3. The cleaning efficiency was calculated using Equation 8-2.



*Figure 8-1:* Bench-scale water shaking incubator.

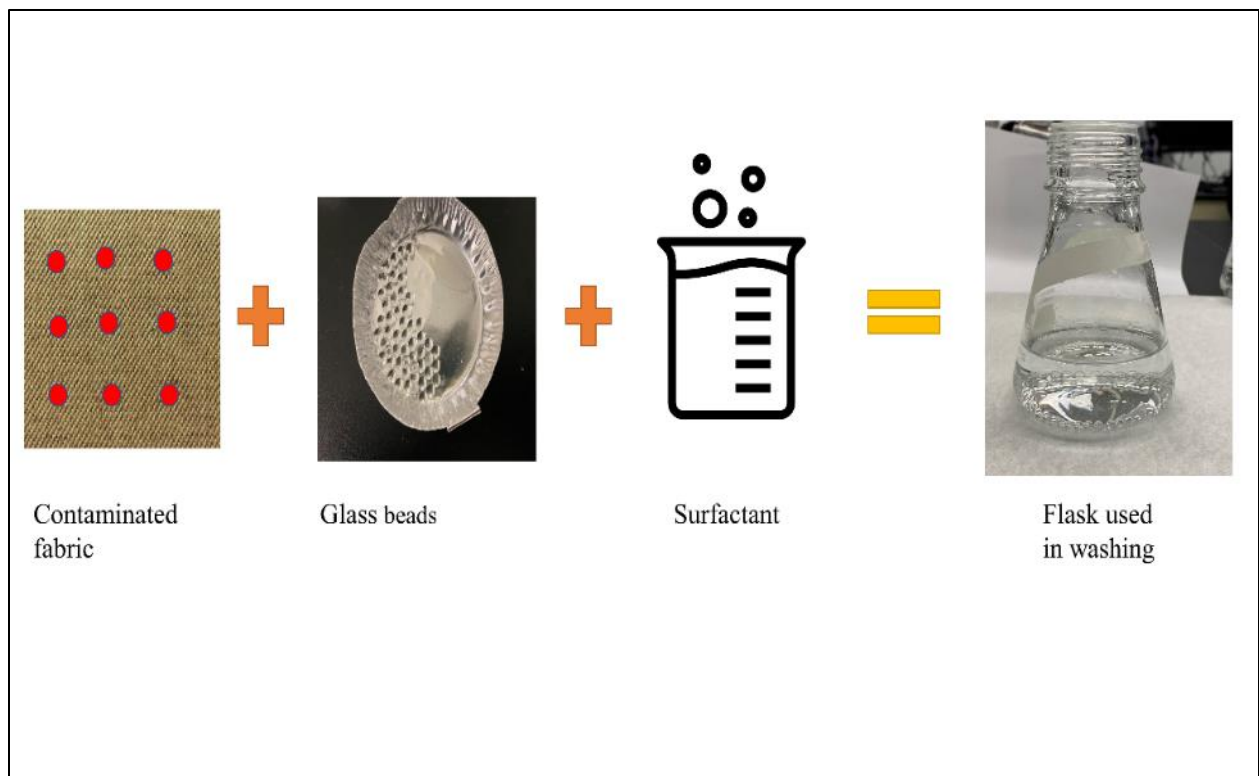


Figure 8-2: Contents in a single washing flask.



Figure 8-3: Process flow for bench-scale washing method.

### 8.3 Results and Discussion

#### 8.3.1 Development of the calibration curve

The calibration curve for the DEHP is shown in Figure 8-4. The correlation coefficient ( $R^2$ ) of 0.999 indicated a strong linear relationship between the concentration and the area under the curve for the compound. The short analysis time for nine compounds allowed for multiple sample analyses. All nine compounds were detected as shown in Figure 8-5. The naphthalene peak in the chromatogram was present since it was added in the custom mix for different research.

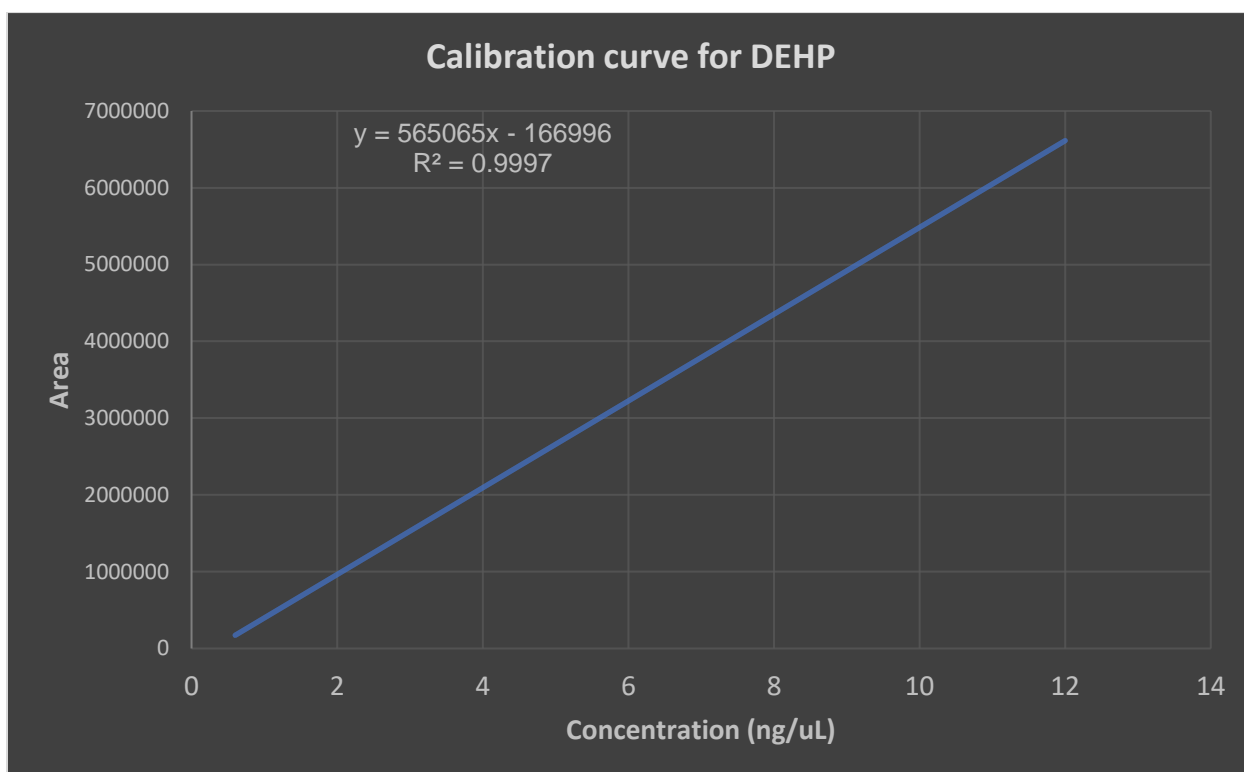


Figure 8-4: Calibration curve for DEHP.



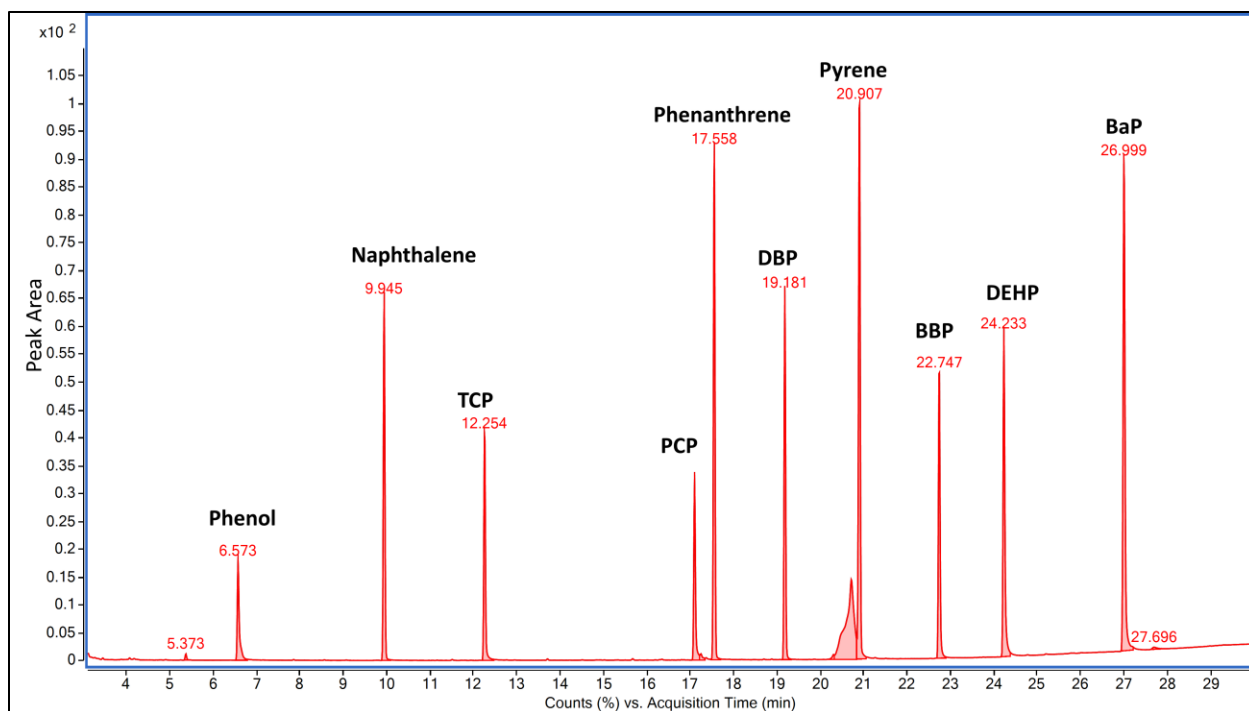


Figure 8-5: Chromatogram of all nine targeted contaminants.

The retention times and  $R^2$  coefficients are provided in Table 8-4. Except for phenols, all the compounds show  $R^2$  values of 0.999 indicating a linear relationship between area and concentration. Phenols generate a low response to the current GC-MS method as compared to the other two groups. The polar nature of phenols interfered with n-hexane which is non-polar and the column used was better suited for non-polar contaminants such as PAHs and phthalates.

Table 8-4: Retention time and linear coefficient of the targeted contaminants.

<b>Compound</b>	<b>Retention Time (minutes)</b>	<b>R<sup>2</sup> Coefficient</b>
<b>Phenol</b>	6.60	0.998
<b>2,4,6-TCP</b>	12.259	0.997
<b>PCP</b>	17.100	0.992
<b>Phenanthrene</b>	17.55	0.999
<b>Pyrene</b>	20.90	0.999
<b>BaP</b>	26.99	0.999
<b>DBP</b>	19.18	0.999
<b>BBP</b>	23.74	0.999
<b>DEHP</b>	24.226	0.999

The LOD and LOQ values are displayed in Table 8-5. The phenols have higher detection limit values as compared to the other two groups. Thus, the low LOQ values for PAHs and phthalates indicate better sensitivity to the used method and the compounds can be quantified even at low concentrations. The average values for LOQs for phenols, PAHs, phthalates are 278.67 ng/cm<sup>2</sup>, 141.33 ng/cm<sup>2</sup>, 125.34 ng/cm<sup>2</sup> respectively. The low LOQ values will be beneficial in the calculations of the washing efficiency of any method. The low end of the calibration curve is more significant for post-washed samples since the goal of any cleaning method is to maximize cleaning efficiency that indicates the lowest amount possible on the washed sample.

Table 8-5: Detection limits for GC-MS analysis using n-hexane.

Compound	LOD		LOQ	
	ng/ $\mu$ L	ng/cm <sup>2</sup>	ng/ $\mu$ L	ng/cm <sup>2</sup>
<b>Phenol</b>	0.29	116	0.9	360
<b>2,4,6-TCP</b>	0.17	68	0.52	208
<b>PCP</b>	0.22	88	0.67	268
<b>Phenanthrene</b>	0.22	88	0.67	268
<b>Pyrene</b>	0.07	28	0.21	84
<b>BaP</b>	0.06	24	0.18	72
<b>DBP</b>	0.09	36	0.26	104
<b>BBP</b>	0.1	40	0.3	120
<b>DEHP</b>	0.13	52	0.38	152

### 8.3.2 Extraction Efficiency

The average extraction concentration (ng/ $\mu$ L) of three fabrics and positive controls is displayed in Table 8-6. The lowest extraction for positive control is for phenol. The concentration spiked was 10 ng/ $\mu$ L. Except for phenols, the concentration values obtained for positive controls for all the compounds were greater than 10 ng/ $\mu$ L. This might be because the concentration of 10 ng/ $\mu$ L lies on the upper end of the calibration curve. Thus, the addition of intercept to the area increases the final value to a greater extent giving the higher concentration. For, TCP, the positive control value was higher that may attribute towards the artifact. The values for PAHs and phthalates are in the AOAC acceptable range [192].

Table 8-6: Amount retrieved from the positive control and fabric.

	<b>Positive Control (ng/μL)</b>	<b>Fabric (ng/μL)</b>	<b>Extraction Efficiency</b>
<b>Phenol</b>	5.64	3.13	56.3
<b>2,4,6-TCP</b>	16.01	14.81	92.3
<b>PCP</b>	13.49	13.02	96.6
<b>Phenanthrene</b>	10.74	9.88	91.3
<b>Pyrene</b>	10.57	10.60	100
<b>BaP</b>	11.38	10.21	89.6
<b>DBP</b>	11.17	10.24	91.6
<b>BBP</b>	13.07	11.92	91
<b>DEHP</b>	13.43	12.29	91.3

The extraction efficiencies of the targeted contaminants are shown in Figure 8-6. Phenols solubilize better in polar solvents such as methanol, ethanol, or acetone. The n-hexane was chosen as solvent since most of the targeted contaminants were non-polar. The extraction efficiency increased as the polarity of phenols decreased ( $K_{OW}$  values of phenol (1.5), 2,4,6-TCP (3.69), PCP (5.12)). The recoveries of phenols from the substrate also depend on temperature and extraction cycle duration. A longer extraction cycle and higher temperature increase the chance of oxidization of phenol compounds and decrease the yield of phenolics in the extracts [193]. The short condensation coils were used in the extraction experiment to limit the precipitation in the lines hence the extracts came out hotter than usual. This may have contributed to the loss of phenol since it had a lower boiling point. This is evident from the large error bar for the compound phenol itself.

The non-polar nature of phthalates and PAHs helped in the higher extraction of these compounds from the fabric into the solvent. For phthalates, the average extraction efficiency is greater than 90%. The three phthalates have boiling points between 300°C to 400°C in increasing order from DBP to DEHP. Thus, the extraction conditions of the method work in favor of removing phthalates from the fabric. Similarly for PAHs, the boiling point increases from phenanthrene to BaP. The boiling point of PAHs is high and hence they are stable at and pressure conditions. The high boiling point of BaP (495 °C) can be a reason for the slightly low extraction efficiency for the compound. The amount present on the fabric is high and hence in given extraction conditions total amount may not be transferred completely from the fabric.

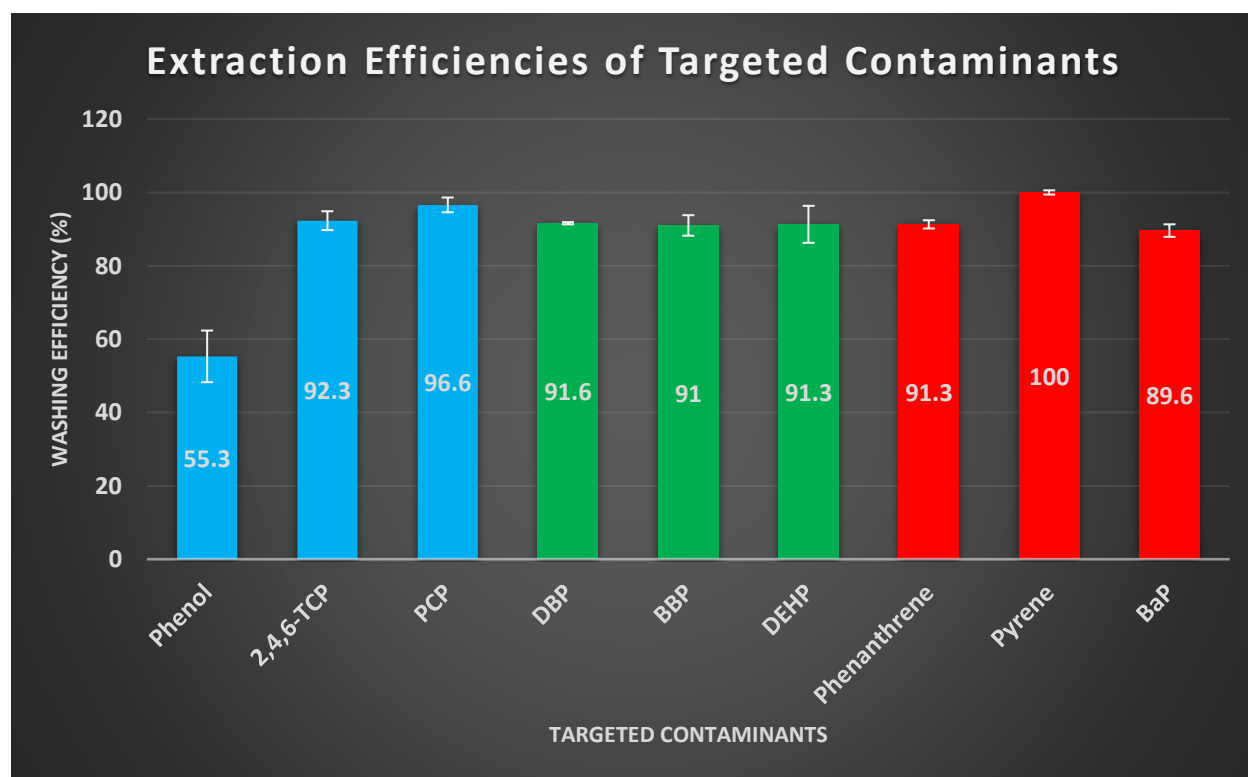


Figure 8-6: Extraction efficiency of the targeted contaminants.

### 8.3.3 Testing variation in bench-scale washing method

The results of the washing for CD-1 and CD-2 are shown in Table 8-7. Every column is the average of three samples per day for two different surfactants. The washing efficiency over the days for both the surfactants is shown in Figure 8-7.

Table 8-7: Average washing efficiencies (%) of the surfactants.

Compounds	CD-1			CD-2		
	Day1	Day2	Day3	Day1	Day2	Day3
Phenol	95.50	95.50	95.50	95.50	95.50	95.50
2,4,6-TCP	97.40	97.40	97.40	97.40	97.40	97.40
PCP	96.65	96.65	96.65	96.65	96.65	96.65
Phenanthrene	79.29	79.39	79.06	80.45	80.34	80.44
Pyrene	46.37	51.30	51.22	49.53	46.52	53.70
BaP	22.83	22.06	14.92	23.55	24.01	30.76
DBP	53.03	54.01	55.33	54.78	51.09	53.95
BBP	34.71	32.67	28.29	25.73	25.03	28.07
DEHP	18.73	16.43	9.93	9.94	8.14	12.54

The average washing efficiency of phenols was calculated using LOQ/2 values due to the absence of chromatograms in the post-washed samples. Based on the LOQ/2 values the maximum washing efficiencies are displayed in Table 8-8. The extraction efficiency for the phenol compound was lower as seen from Figure 8-6. When the value of extraction efficiency was taken into account for phenol, the washing efficiency for phenol was still greater than 90% as the LOQ/2 value of phenol was 55.6% of 0.81ng/ $\mu$ L. Since the chromatograms of phenols

were not present in the post-washed samples, the LOQ/2 values were taken without the calculation of extraction efficiency. The average washing efficiencies are illustrated in Figure 8-7. The washing efficiencies for both the surfactants are consistent across three days. The phenols are washed out effectively using both the surfactants.

The interesting trend observed here is within any chemical group, the average washing efficiency decreased as the polarity of the compounds decreased. Thus, a declining trend is observed from phenanthrene to BaP and DBP to DEHP. The contamination spiked on each fabric was 4000 ng/cm<sup>2</sup>. The average contamination present after washing is shown in Figure 8-8. The bench-scale washing experiment illustrated the interesting correlation between the polarity of the contaminants and the solvent. For the extraction experiment, phenols displayed poor response due to the n-hexane while the other two groups were removed satisfactorily. For the washing experiment, water was used as a cleaning solvent and the trend was reversed. Compounds such as DEHP, BaP were present in amounts greater than 3000 ng/cm<sup>2</sup>. This was consistent with both the surfactants. This warranted a further investigation into the effects of various parameters on cleaning efficiency.

Table 8-8: Maximum washing efficiency.

<b>Compound</b>	<b>LOQ/2</b>	<b>Maximum Washing Efficiency (%)</b>
<b>Phenol</b>	0.45	95.50
<b>2,4,6-TCP</b>	0.26	97.40
<b>PCP</b>	0.335	96.65
<b>Phenanthrene</b>	0.335	96.65
<b>Pyrene</b>	0.105	98.95
<b>BaP</b>	0.09	99.10
<b>DBP</b>	0.13	98.70
<b>BBP</b>	0.15	98.50
<b>DEHP</b>	0.19	98.10



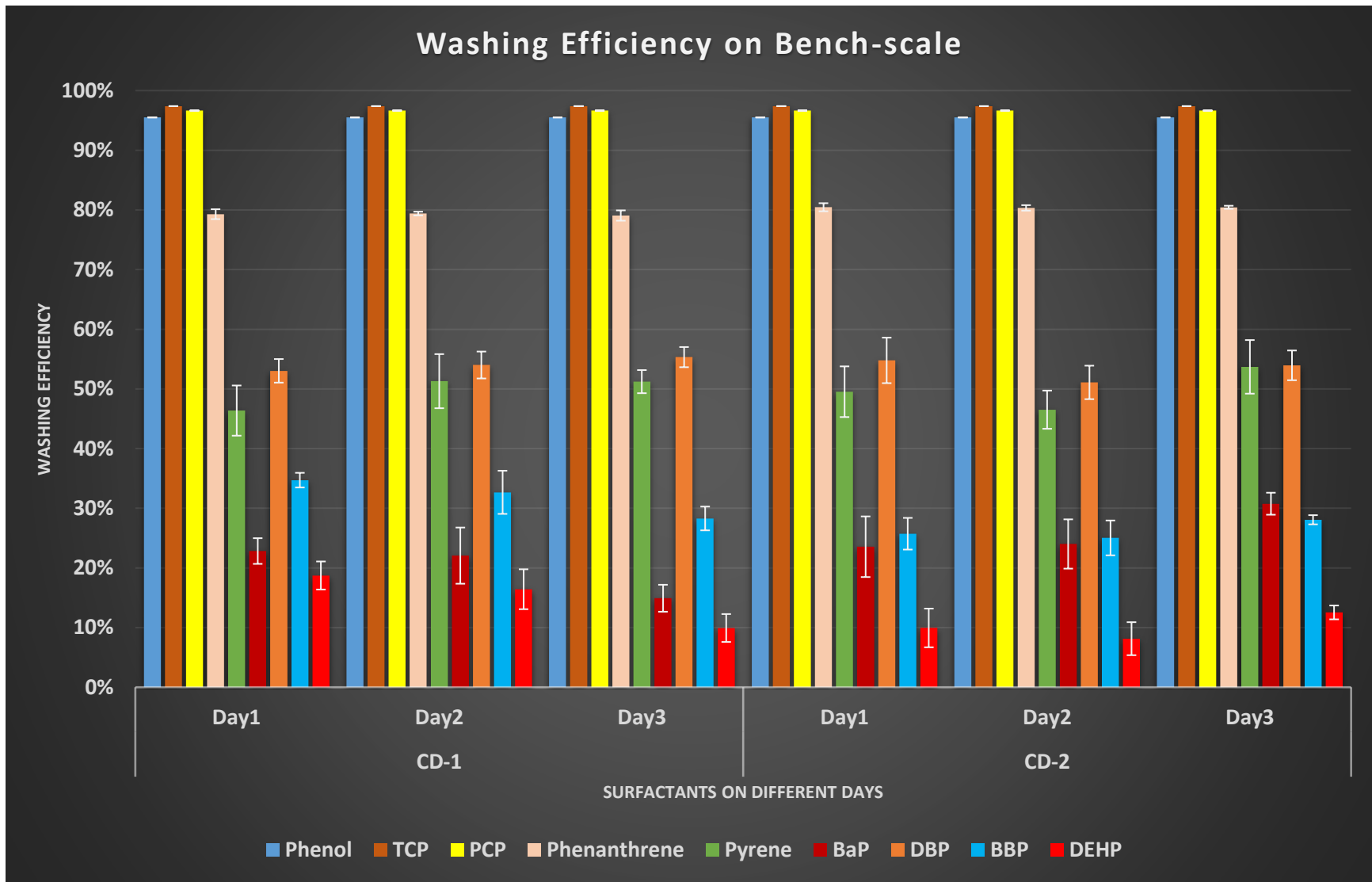


Figure 8-7: Consistency of the bench-scale washing method.

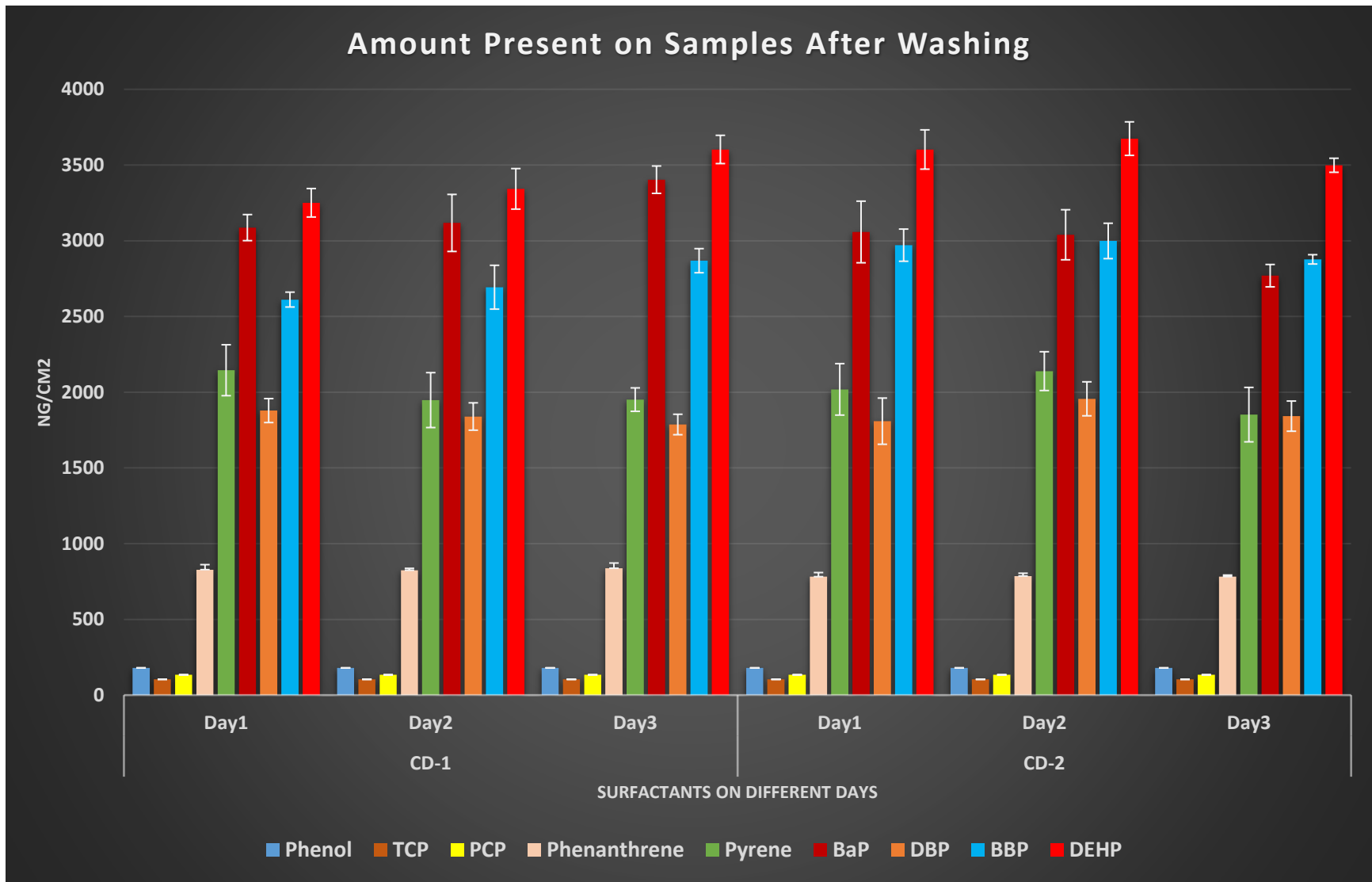


Figure 8-8: Average contamination present on samples after washing.

To check the variation in the procedure over three days, one-factor ANOVA was used within days. The p-value was set for 0.05. The analysis for CD-1 and CD-2 was shown in Figure 8-9 and Figure 8-10, respectively. The p-value is greater than 0.05 which indicates that there is no statistical difference, and we fail to reject the null hypothesis: means of washing for different days for the same surfactant is equal. This proved that the bench-scale washing is consistent, and it was ready to be used in our further experiments.

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		
Column 1	9	5.274545	0.586061	0.089575		
Column 2	9	5.283698	0.587078	0.092623		
Column 3	9	5.112474	0.568053	0.109589		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.002062	2	0.001031	0.010599	0.989461	3.402826
Within Groups	2.334295	24	0.097262			
Total	2.336357	26				

Figure 8-9: ANOVA testing for CD-1.

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		
Column 1	9	5.164913	0.573879	0.10443		
Column 2	9	5.076266	0.56403	0.107724		
Column 3	9	5.319606	0.591067	0.093318		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00337	2	0.001685	0.01655	0.983597	3.402826
Within Groups	2.44377	24	0.101824			
Total	2.447141	26				

Figure 8-10: ANOVA testing for CD-2.

#### 8.4 *Conclusion*

The bench-scale method development part included three steps. The initial step was the development of the GC-MS method. The calibration curve provided a range of concentrations that would be beneficial for both pre-wash and post-wash sample quantitative analysis. The contaminants in solvent n-hexane demonstrated high sensitivity thus generating very low detection limits. When considered from the cleaning perspective, these values enable calculating cleaning efficiency close to 99 %. Thus, the low end of the calibration curve was more crucial. The short duration of 30 minutes for the GC-MS method accelerated multiple sample analysis.

The extraction step is the intermediate step and it demonstrated that the fabric holds the contaminants. The extraction efficiencies were high for six out of nine compounds. The boiling point and non-polarity of the samples affect extraction efficiencies. The method was more suitable for PAHs and phthalates as compared to phenols. The consumption of solvent was low that made the method efficient and economical. The bench-scale experimental procedure as seen from the results was consistent and met the project objectives. The n-hexane was compatible with most of the targeted compounds due to its non-polar nature.

The bench-scale washer-extractor could hold a maximum of nine samples in one batch. This facilitated the use of three replicates for one single bench-scale washing experiment. The data obtained using the bench-scale washing method was consistent for both commercial detergents. The phenols demonstrated high cleaning efficiency as compared to PAHs and phthalates. The washing experiments on the bench-scale level have low chances of cross-contamination that increased the credibility of the data. This made the bench-scale washing experiments reliable and repeatable. The cleaning efficiency of the contaminants decreased as the non-polarity of the contaminants increased. This displayed their affinity towards the fabric.

The choice of solvents had a significant impact on removing the contaminant from the fabric. Both the surfactants used demonstrated comparable washing efficiencies for all the targeted contaminants. Thus, the investigation of the effect of different washing parameters on cleaning efficiency was executed in the next studies.

## **Chapter 9: Evaluation of Washing Parameters on Bench-scale Washing and Comparative Analysis on Full-Scale Washer Extractor**

### **9.1 Introduction**

Occupational chemical exposure is one of the probable causes of firefighters having higher incidences of respiratory disease, heart disease, and cancers than the general population [194]-[197]. During fire suppression activities, firefighters are exposed to a variety of chemicals that include polycyclic aromatic hydrocarbons (PAHs) and phthalates among many other classes of compounds [8]. PAHs are formed due to the incomplete combustion of materials and phthalates are ubiquitously used as plasticizers [38].

Limited research has been conducted on the effectiveness of the laundering practices used by the firefighting community, with the available results indicating high variability across the targeted compounds. Using a brush with soap and water for on-scene decontamination, Fent et al. showed there was an 85% reduction in total PAH concentration through wipe sampling of the turnout gear before and after the decontamination procedure, while only a 23% reduction was shown using a dry-brush technique [11]. Using water-only decontamination, Calvillo et al. found a 42% increase in PAHs concentration on structural firefighting uniforms, however, the increase between pre and post-wash samples could be due to disparate locations used for sample collections. The forearm and shoulder areas were selected for sample collections. The spatial variability in these locations and the unknown efficiency of the wipes may have contributed to the increase in concentration after decontamination [10]. Similar studies showed variation in concentration in pre and post-laundering samples [9], [198]. The small sample size, spatial variation due to uneven contamination made the analysis of the washing practices incomplete.

Fire departments laundered their gear for a more complete decontamination process. Firefighters wash their gear at different time intervals and there are so many variables involved such as different temperatures, time, detergent, etc. Clearly, there is a lack of information about how the various parameters such as temperature, time, and surfactants affect the removal of contaminants.

The following study evaluated various washing parameters on the bench-scale method described in Chapter 8:. Using a design of experiments (DOE) approach, washing was performed on the bench-scale and the effect of multiple washing parameters was assessed. The second part of this study focused on evaluating how well the bench-scale approach replicated the results from the full-scale washer extractor.

### ***9.2 Experimental design for evaluating the effect of washing parameters on the cleaning efficiency on the bench-scale***

The primary objective of this study was to evaluate the impact of washing parameters on the cleaning efficiency of turnout gear materials when performed according to the NFPA 1851 standard. These parameters include detergents being used by firefighters as well as washing temperature duration. The NFPA 1851 standard has prescribed some guidelines that contain the important constraints: (1) Temperature should not exceed 40°C; (2) the pH of the detergent should be between 6-10.5 and should not contain chlorine bleaching agents or any oxidizing agents; and (3) the G-force for machine cleaning should be less than 100 G. Considering all the constraints, the experimental design was performed using the JMP pro15 software. The important parameters considered were temperature, washing duration (time), and surfactant as shown in Table 9-1. Of these three parameters, time and temperature are continuous variables while surfactant was considered as categorical. The design was full factorial and contained



random sampling. Every experiment was performed in triplicate; hence the total number of experiments was 24. The goals were: (1) To evaluate the cleaning efficiency of washing according to NFPA 1851. (2) To study the effect of variation in temperature, washing duration, and surfactant choice on cleaning efficiency.

Temperatures: 40°C was chosen since that was the upper limit for washing according to the NFPA 1851 standard. The 65°C was added to study the effect of higher temperature on removing contaminants.

Time: There is no particular constraint on the washing duration, but different Independent Service Providers have different washing durations. Hence to study the effect of the short washing cycle and long washing cycle, the 15 mins and 60 mins cycles were added.

Surfactants: The commercially available detergents (CD): CD1 and CD2 were chosen since both were used in the validation of the bench-scale method. Also, CD1 is a popular surfactant in the firefighting community and CD2 is the regular home laundry surfactant. Choosing these would help in understanding provide the effect of different surfactants on removing different contaminants. The different ingredients for the surfactants are provided in Table 9-2

*Table 9-1: Parameters for the design of experiments.*

<b>Surfactants</b>	<b>Temperature (°C)</b>	<b>Time (minutes)</b>
<b>CD-1</b>	40	15
<b>CD-2</b>	65	60

Table 9-2: Ingredients for CD1 and CD2.

CD-1	CD-2
D-Limonene	Non-ionic surfactant, Alcohol ethoxylate
Non-ionic surfactant: 4-Nonylphenyl-polyethylene glycol	Anionic surfactant: Alkyl ethoxy sulfate and alkyl sulfate, linear alkylbenzene sulfonate
Mackamide C	Amine oxide
Glycol ether	Hydrogen peroxide
	Percarbonate

### 9.3 *Bench-scale washing method*

The process of the bench-scale washing method was similar to the validation experiments as described in Section 8.2.4. The level of contamination for all the targeted contaminants was 60000 ng on each swatch. This level of contamination was chosen at 60000 ng since the amount of contaminant present on the fabric was 2400 ng/cm<sup>2</sup> that was in the middle of the calibration curve (Table 8-2) and to save the resources. The mid-point of the calibration curve would help in reducing the deviations that might occur at larger concentrations.

### 9.4 *Full-scale washing method*

A primary objective of the research was to assess how well the bench-scale washing method compared to the full-scale washer-extractor used in fire departments and independent service providers (ISPs). Thus, for this section, a design of experiments similar to the bench-scale washing Table 9-1 was employed for full-scale testing.

#### 9.4.1 Sample Preparation

Five unused turnout jackets were modified to have hook-and-loop swatches placed in strategic locations on the jacket to hold the test fabric swatches as shown in Figure 9-1. In total eight patches were stitched: four on the front torso, one on each sleeve, and two on the back that were capable of holding test samples. The hook part was stitched onto the outer shell material of the jackets while the loop part was stitched to the test samples. The study was limited to evaluating the outer shell material only. For this set of experiments, only five of the swatch locations were used due to limited resources. The locations for the swatches were chosen randomly but in every experiment, atleast one swatch was located on the sleeve and one on the back of the garment.



Figure 9-1: Velcro patches on the uncontaminated jackets.

The test samples (5 cm x 5 cm) were cut from a new roll of PBI Max™ Gold (7 oz.) and were contaminated with the master mix of fireground contaminants according to the protocol described in Subsection 8.2.4 for the bench-scale procedure. The level of contamination was 60000 ng to maintain uniformity with the bench-scale DOE. An example of a test jacket with the contaminated test swatches affixed is shown in Figure 9-2.



*Figure 9-2: Final product for washing.*

#### *9.4.2 Full-scale extractor method*

The washer-extractor used was a UNIMAC 45 lb. (Model no-UWT045D4). The machine was fully programmable for temperature and washing duration. The parameters for DOE were similar as described in Table 9-1. The jacket with contaminated swatches was placed in the washer-extractor along with the ballast material. The ballast material included unused outer shell garments and unused inner layers. The surfactant was added in a separate compartment. The parameters for a particular washing experiment were pre-programmed using the laptop into the

machine. For all the washing experiments, a separate rinse cycle of 10 mins was added just to simulate the bench-scale washing. In this cycle, all the water was drained, and the samples were rinsed with fresh water. After washing, the jacket with samples was removed and air-dried. The loop part of the hook-and-loop was removed from the test swatches and the samples were analyzed using the extraction and analysis methods described in Section 8.2.3. To mitigate cross-contamination, all the jackets and ballast materials were washed again in-between the experiments.

The recommended dosage for CD1 was 180 mL for 45 lbs. load. The total load including the ballast material for every single wash was 30 lbs. The dosage calculated for the load of 30 lbs. was 120 mL. Hence, a similar amount was taken for CD2 since the MSDS did not provide any recommended amount for CD2.

## 9.5 *Results and Discussion*

### 9.5.1 *Bench-scale evaluation of the various washing parameters*

The average washing efficiencies of the targeted contaminants are shown in Figure 9-3. For the combination CD2-40-15, data for two swatches were displaying outliers due to experimental artifacts. The washing efficiency of the phenol compound is calculated using the LOQ/2 values. The common trends across all combinations that were evident from the data were:

- (1) Average washing efficiencies for phenols were higher as compared to PAHs and phthalates.
- (2) Within a chemical group, the washing efficiency decreased as the  $K_{OW}$  value increased.

Thus, for PAHs washing efficiency decreased from phenanthrene to BaP and for phthalates, it decreased from DBP to DEHP. Even for phenols, a similar trend was observed. This suggested that the polarity of the cleaning solvent played a significant role in the removal of contaminants from the fabric.

To study the effects of variation in parameters, the analysis of all the data was performed using JMP pro15. The fit model test was incorporated for individual analysis of the contaminants.

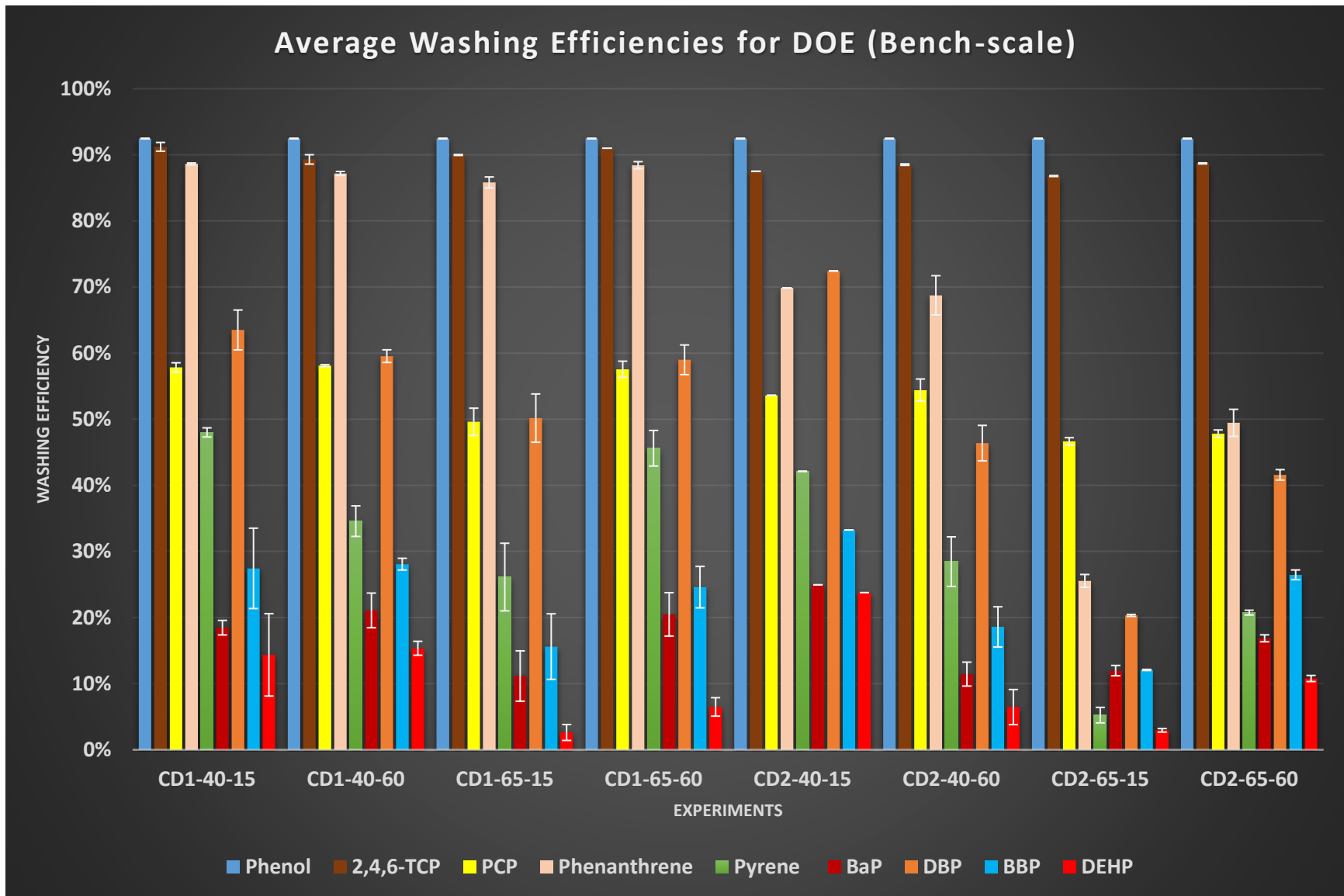


Figure 9-3: Average washing efficiencies for different combinations of parameters (Bench-scale).

The summary of effects of various parameters is given in the following Figure 9-4. The LogWorth value is the negative logarithmic value of the p-value:  $-\log_{10}(\text{p-value})$ . A LogWorth value greater than 2 of an effect indicates that the effect has a significant impact at  $p=0.01$  level thus indicating the importance of all the parameters on the removal of compounds. The p-value is a probability value that describes how likely the data would have occurred randomly. Thus, a high LogWorth value indicated a very low probability of random results generated or the effect could have occurred by chance. The summary showed that all the parameters and their cross effects have a significant impact on removing compounds when they are considered together in the mix. The chemistry of different functional groups and competitive effects of the chemicals need to be considered for the removal of contaminants from the same mix. The effect summary shown below (Figure 9-4) is for all the chemicals in the mix. The surfactant displayed a high LogWorth (11.92) value as compared to the. The difference was significant when compared with LogWorth values of other parameters. This high value indicated that the chemistry of contaminants with surfactants played a significant role in the removal of contaminants from the fabric. Thus, the choice of surfactants was a very important parameter while removing the targeted contaminants when considered all together in a mix. The mix contained targeted contaminants from three different classes thus indicating that the chemical nature of the contaminants needed to be studied while deciding the washing parameters. The effect summary for individual classes PAHs, phthalates, phenols are shown in Figure 9-16, Figure 9-17, Figure 9-18 respectively.



Source	LogWorth		PValue
Surfactants	11.923		0.00000
Temperature(40,65)	7.705		0.00000
Surfactants*Temperature	7.419		0.00000
Temperature*Time	4.897		0.00001
Time(15,60)	2.949		0.00113
Surfactants*Time	2.654		0.00222
Surfactants*Temperature*Time	2.626		0.00237

Figure 9-4: Effect summary for the entire mix (bench-scale).

Source	LogWorth		PValue
Surfactants	11.923		0.00000
Temperature(40,65)	7.705		0.00000
Surfactants*Temperature	7.419		0.00000
Temperature*Time	4.276		0.00005
Time(15,60)	2.949		0.00113
Surfactants*Time	2.654		0.00222
Surfactants*Temperature*Time	2.555		0.00279

Figure 9-5: Effect summary for PAHs (bench-scale).

Source	LogWorth		PValue
Temperature(40,65)	5.694		0.00000
Temperature*Time	4.897		0.00001
Surfactants	4.190		0.00006
Surfactants*Temperature	3.490		0.00032
Surfactants*Temperature*Time	2.626		0.00237
Surfactants*Time	0.722		0.18964
Time(15,60)	0.348		0.44924

Figure 9-6: Effect summary of phthalates (bench-scale).

Source	LogWorth		PValue
Temperature(40,65)	3.875		0.00013
Surfactants	3.331		0.00047
Temperature*Time	1.546		0.02846
Time(15,60)	1.336		0.04615
Surfactants*Time	1.260		0.05499
Surfactants*Temperature*Time	0.868		0.13547
Surfactants*Temperature	0.657		0.22051

Figure 9-7: Effect summary for phenols (bench-scale).

The individual parameters and their effects on different chemical groups are explained in detail below:

#### 9.5.1.1 Surfactants

From the effect summaries, it was evident that the choice of surfactant had a significant impact on the removal of contaminants especially PAHs and phenols. The prediction profile of the PAHs for various parameters is shown in Figure 9-8. The washing efficiency decreases as the number of rings in PAHs increases which is related to the hydrophobicity of the compound [199]. The responses shown in Figure 9-8 indicated that overall CD1 proved to be better than CD2 in removing PAHs. The D-limonene in CD1 is a non-polar compound that was effective in removing PAHs since PAHs have a high octanol-water partition coefficient and are non-polar (Table 8-1). The non-ionic surfactants have been shown to solubilize PAHs effectively [200]. This is consistent with the data since CD1 had a non-ionic surfactant that helped in solubilizing PAHs. For phenanthrene and pyrene, there is a steep decline in washing efficiencies for change in detergent from CD1 to CD2 that denoted that the simple PAHs were more sensitive to change in surfactant. This highlighted that mixed surfactant systems of anionic surfactants and non-ionic surfactants in CD may not be effective in removing PAHs. BaP did not respond positively to any surfactant since it is highly non-polar.

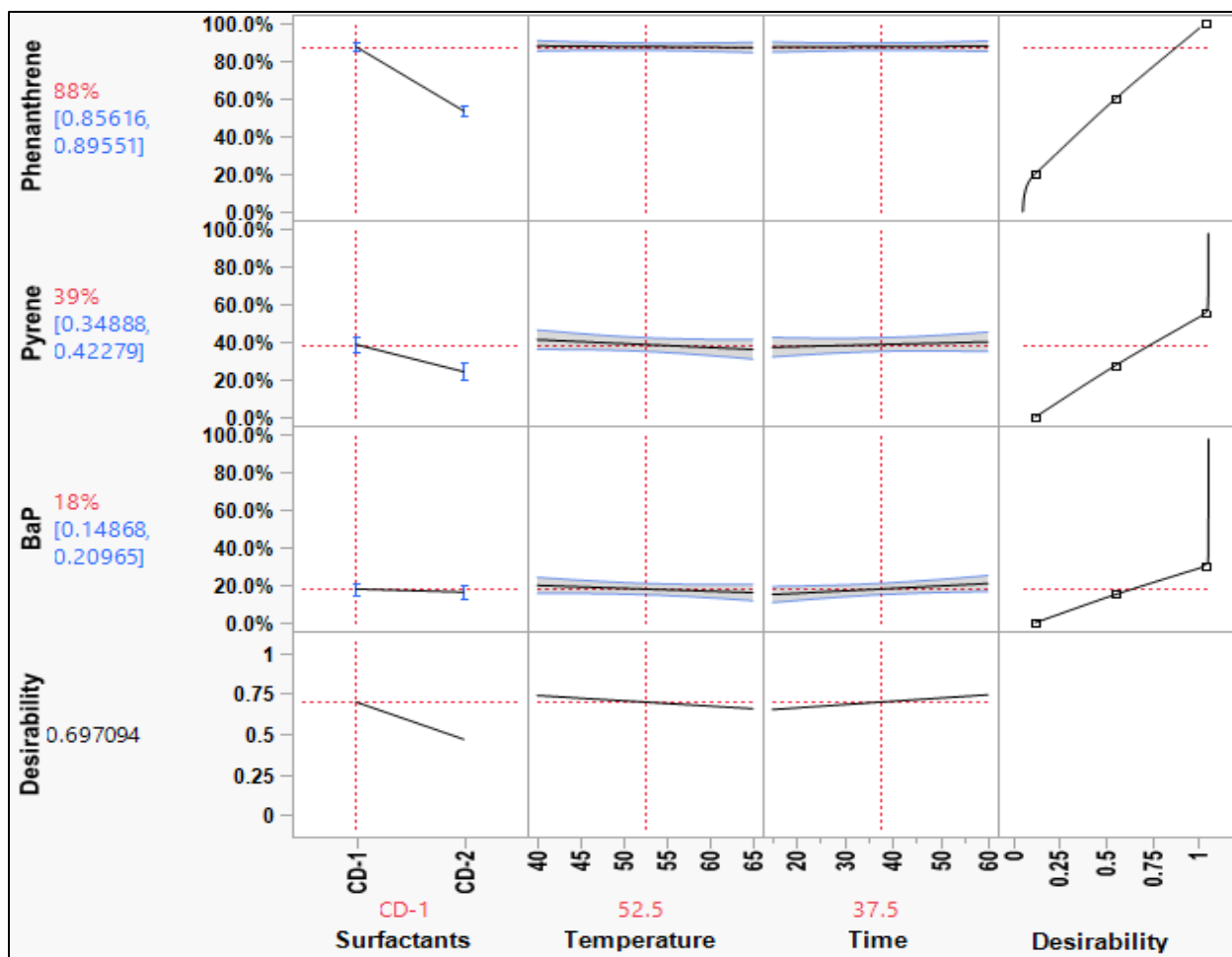


Figure 9-8: Prediction profile for PAHs (bench-scale).

The effect of change in surfactants on the removal of phthalates is shown in Figure 9-9. The overall washing efficiency for phthalates is low as compared to the other groups. Similar to PAHs, the washing efficiency decreased from simple phthalates to complex phthalates. The  $K_{ow}$  value increased as the alkyl chain length increased that indicating an increase in hydrophobicity [76]. The trend of removal of phthalates was similar to PAHs. For a change in surfactant from CD-1 to CD-2, DBP showed a steep declining slope comparatively that notified that simple phthalates such as DBP were sensitive to change in surfactants. The D-limonene and non-ionic surfactant removed simpler phthalates effectively similar to phenanthrene. This indicated that the phthalates will not partition in aqueous solutions easily just by using conventional surfactants.

The hydrophobic cores of surfactant micelles can help in desorbing the hydrophobic compounds, but the lower concentration of surfactant limited the availability of these spaces thus overall washing efficiency was low [202].

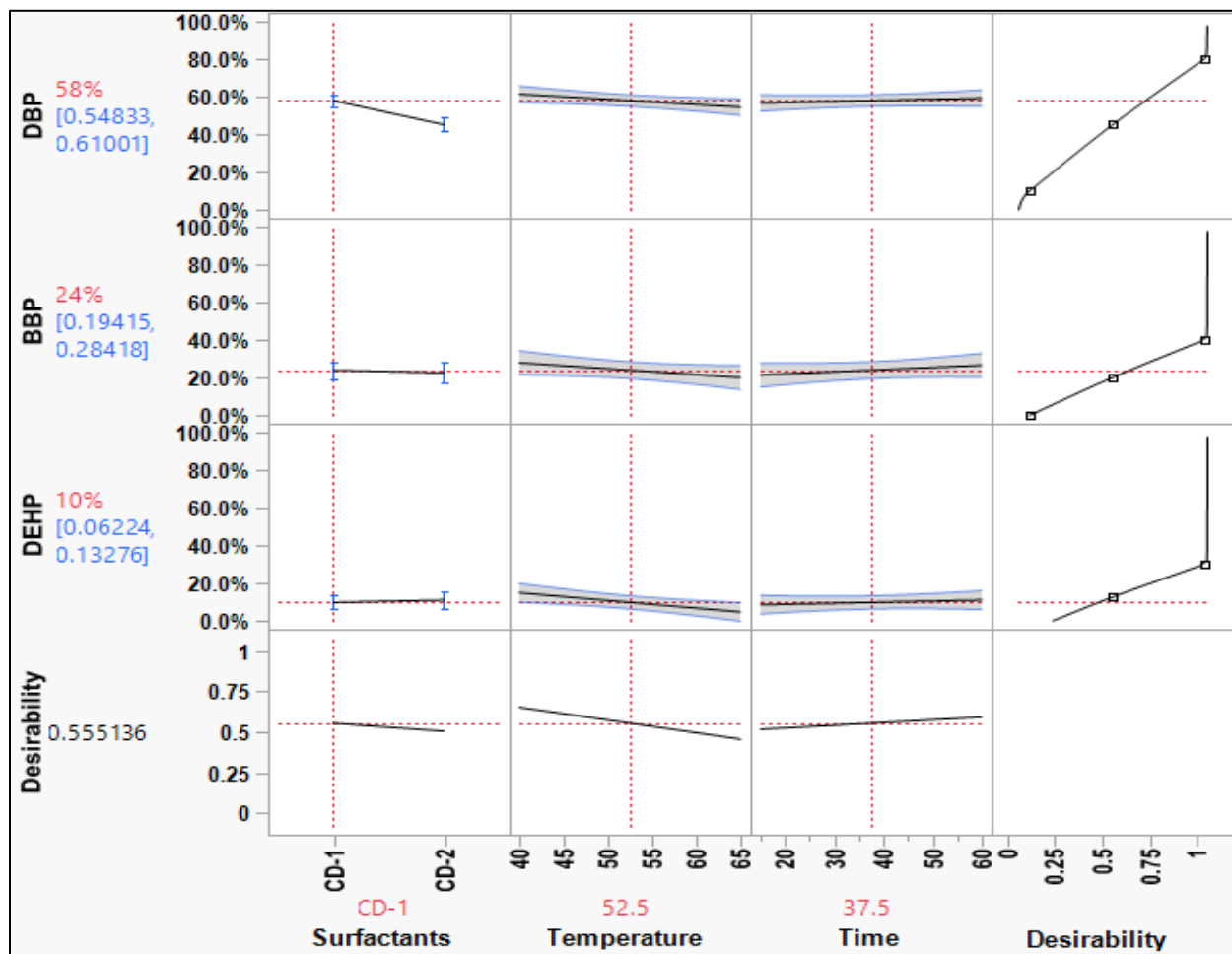


Figure 9-9: Prediction profile for phthalates(bench-scale).

The overall washing efficiency for phenols was high as compared to the other chemical groups since phenols are highly polar Figure 9-10. Phenol compound is moderately soluble in water. The washing efficiency of phenol was calculated using the LOQ/2 value. Thus, phenol was washed out well beyond the detection limits of the analytical method used. Phenols might form soluble salts with surfactants that helped in their removal. The substitutions of compounds on the phenolic ring increase the stability of the ring that increases the hydrophobicity. Hence the

removal efficiency of the chlorinated phenols decreased in the following order: phenol > 2,4,6-TCP > PCP. The results of phenols for surfactant variation in the parameters were fairly consistent.

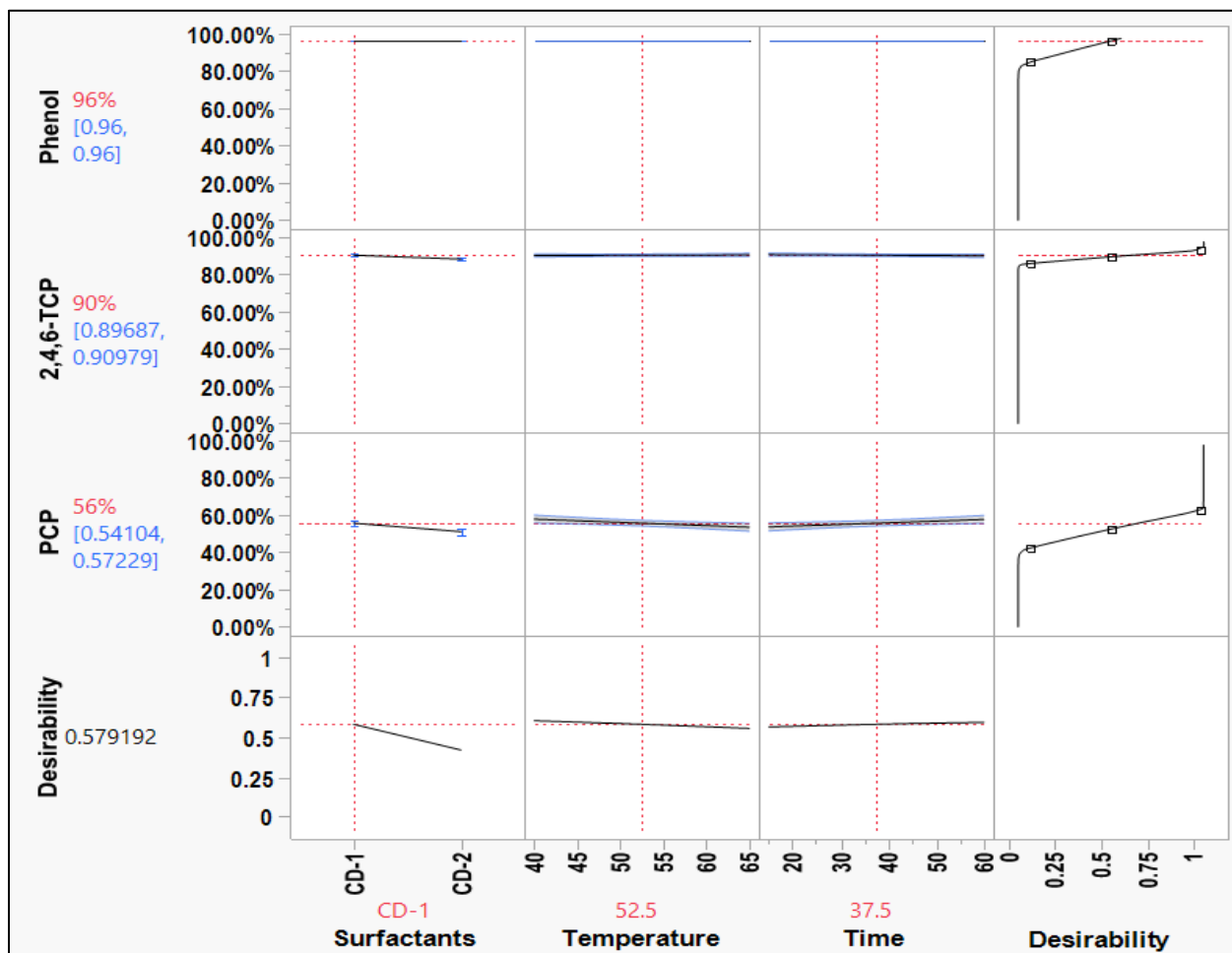


Figure 9-10: Prediction profile for phenols (bench-scale).

### 9.5.1.2 Temperature

The temperature was the second important parameter as seen from the effect summary (Figure 9-4). The prediction profiles alone did not show any significant change in the trends of washing efficiency for the increase in temperature. For, pyrene and BaP a slight decline is observed for an increase in temperature. The effect summary for PAHs showed that the cross effect of surfactant and temperature had a comparable LogWorth value (Figure 9-5). Thus, the

interaction plots displayed in Figure 9-11 highlighted the cross effects of temperature with surfactant and time. The washing efficiency of the CD2 decreased drastically for higher temperatures. The hydrophilicity of the anionic surfactant increased while the reverse effect is generally observed in the non-ionic surfactant by increasing temperature [203]. Hence, the washing efficiency decreased drastically for CD2 when compared to CD1 for an increase in temperature. The higher temperatures did not have any significant impact on removing phenanthrene and BaP. This might be since phenanthrene is a simple PAH and is removed effectively irrespective of the temperature, unlike BaP that is not partitioned easily into the aqueous solution ( $K_{OW}=6.13$ ). This is consistent with the soil washing experiments done on the bench-scale level. The increase in temperature did not improve the contaminant removal [204]. Similar trend was observed in phthalates. The comparable values of LogWorth for phthalates as seen in Figure 9-6 highlighted that all the variables and their cross-effects played an equally significant role in removing them from the fabric. This was primarily because phthalates in the mix had a strong interaction with the fabric as compared to the surfactant solution. The effect of increasing temperature on washing efficiency for phthalates was slightly negative although the results were comparable. The removal of phthalates was consistently low irrespective of the combination of parameters. This indicated that temperature can only benefit if the surfactants are effective in the first place.

For phenols, the interaction plots are shown in Figure 9-24. For phenol and 2,4,6-TCP, the change in the temperature did not affect their removal and demonstrated consistent washing efficiency. So, the solubilization of the phenol and 2,4,6-TCP by forming salts with the counterion of the surfactants was not affected. For PCP, there was a slight decline in washing efficiency. This was the only significant impact temperature had while removing phenols.

Similar to PAHs, the washing efficiency of PCP decreased by increasing the temperature when other parameters are kept constant.

#### *9.5.1.3 Time*

When effect summaries were studied, the effect of time on washing efficiencies was low when the LogWorth values are compared with surfactants and temperature (Figure 9-4). For PAHs, temperature and time had strong interaction. The third column in Figure 9-11 is for the time that highlighted the strong interaction of temperature and time for phenanthrene and pyrene (highlighted in red boxes). For BaP, even surfactants had a strong interaction with time (box highlighted in green). The effect of CD1 increased for longer washing durations. This is consistent because the hydrophobicity would take time to desorb BaP from the fabric. Although the individual effect of time was negligible due to low LogWorth value as illustrated in the effect summary for phthalates (Figure 9-6) there is a negative effect of time on the removal of phthalates. The primary reason can be seen in the interaction plots (Figure 9-12) for the cross-effect of surfactant and time (highlighted in green). CD2 worked better in removing phthalates as compared to CD1 for 15 minutes washing but is unable to prevent redeposition of phthalates on the fabric surface for longer washing durations. The effect of time on CD1 is negative for the removal of DBP which indicated that DBP started redepositing for longer washing durations. Although higher temperature and longer washing time together (highlighted in red) showed a positive slope for removal of phthalates, the removal efficiency values did not increase above 50%. This showed for phthalates, there is a very limited scope in their removal using conventional surfactants in aqueous washing given their superhydrophobic nature. Even longer washing durations didn't make any significant improvement on removing phthalates effectively that concludes that aqueous washing using these surfactants even at longer washing durations is

at a limit in removing phthalates from the fabric. Thus, better surfactants are needed for the removal of phthalates.

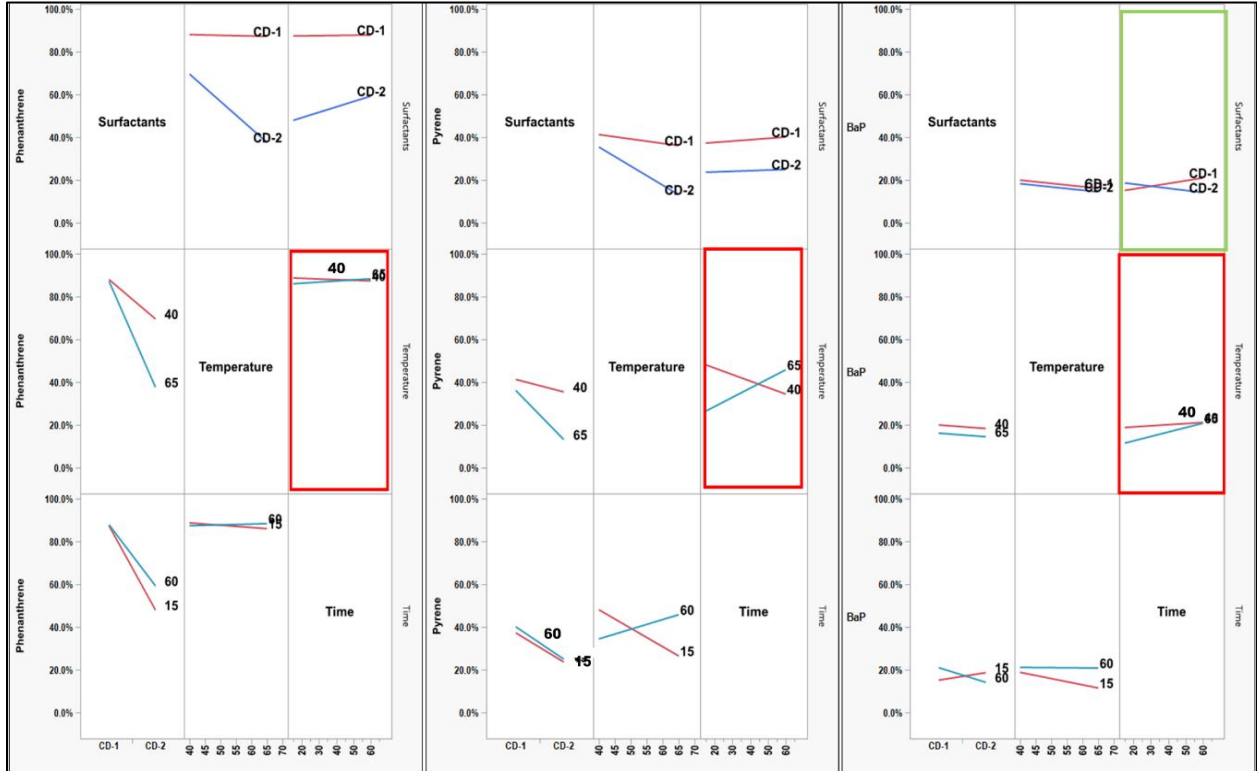


Figure 9-11: Interaction plots for PAHs (Bench-scale).



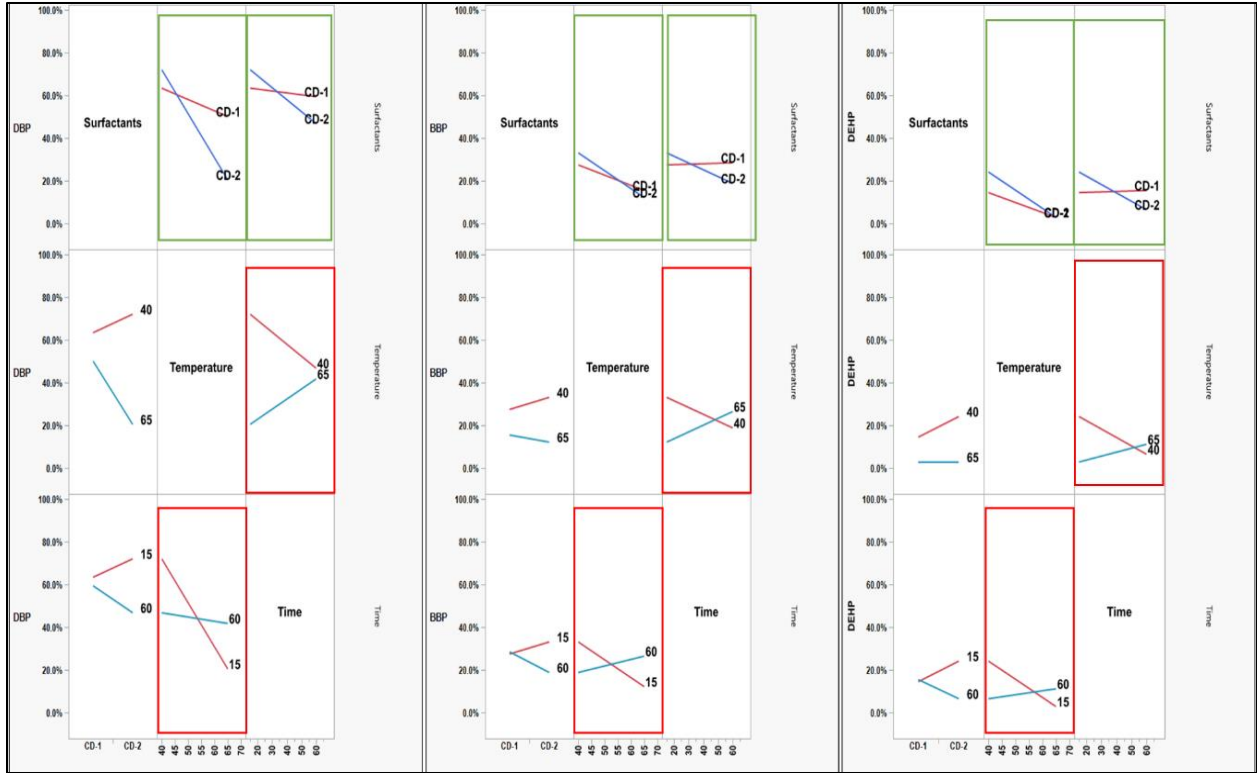


Figure 9-12: Interaction plots for phthalates (Bench-scale).

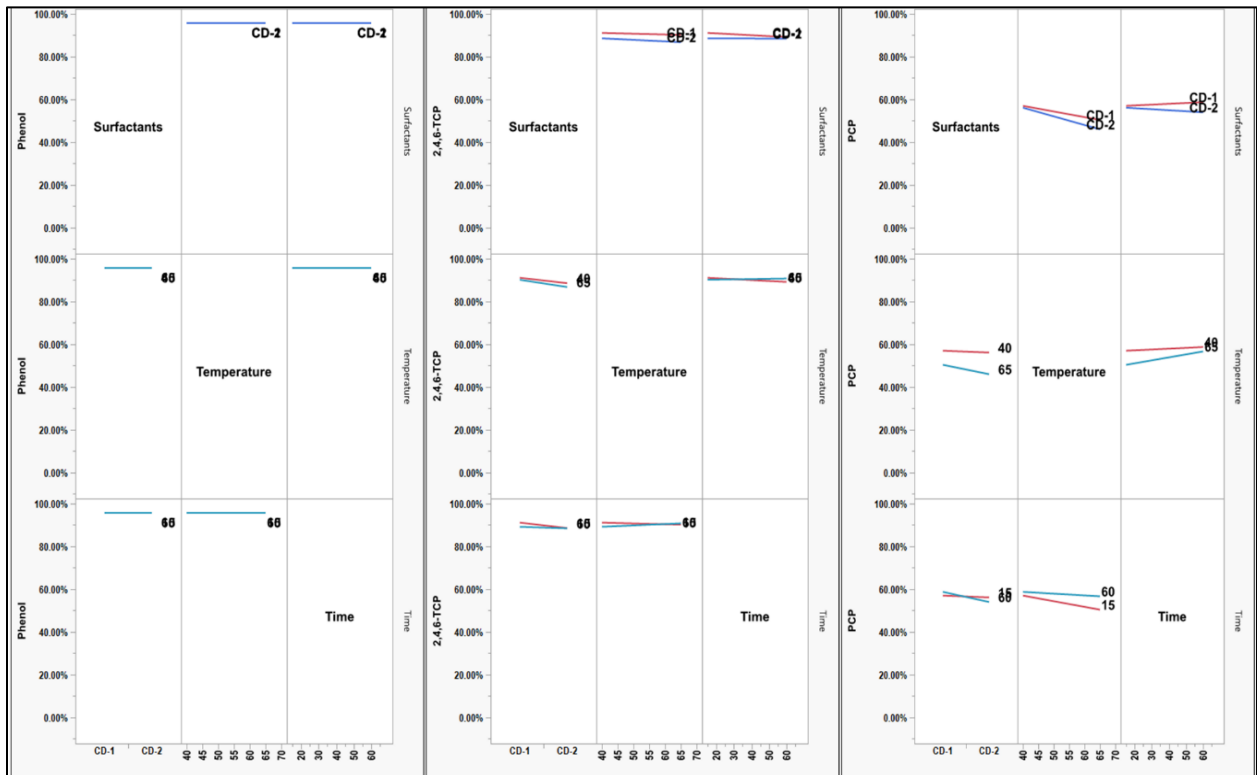


Figure 9-13: Interaction plots for phenols (Bench-scale).

### 9.5.2 *Comparative analysis with full-scale washing*

The implementation of full-scale washing was to further evaluate the effects of temperature on washing and understand how it is different from the bench-scale washing experiments. The average washing efficiencies for full-scale DOE are shown in Figure 9-14. Similar to the bench-scale level, phenols demonstrated higher washing efficiencies as compared to the PAHs and phthalates. The washing efficiency of phenol, 2,4,6-TCP were calculated using the LOQ/2 values. The trend of decreasing washing efficiencies as the  $K_{OW}$  values increased was also consistent in both levels. Similarly, washing efficiencies for BaP and DEHP were consistently low for full-scale washing that was also observed in bench-scale washing. The values for phenanthrene and DBP in full-scale washing were comparable with those for bench-scale washing. This showed that common trends in chemical groups for full-scale washing can be correctly predicted using bench-scale washing. The average washing efficiencies for all the compounds were higher in full-scale washing when compared with the bench-scale. This indicated that the mechanical agitation in full-scale washer-extractor may have contributed to the removal of contaminants.

The JMP Pro 15 was used to perform a statistical analysis to assess the effect of parameters.

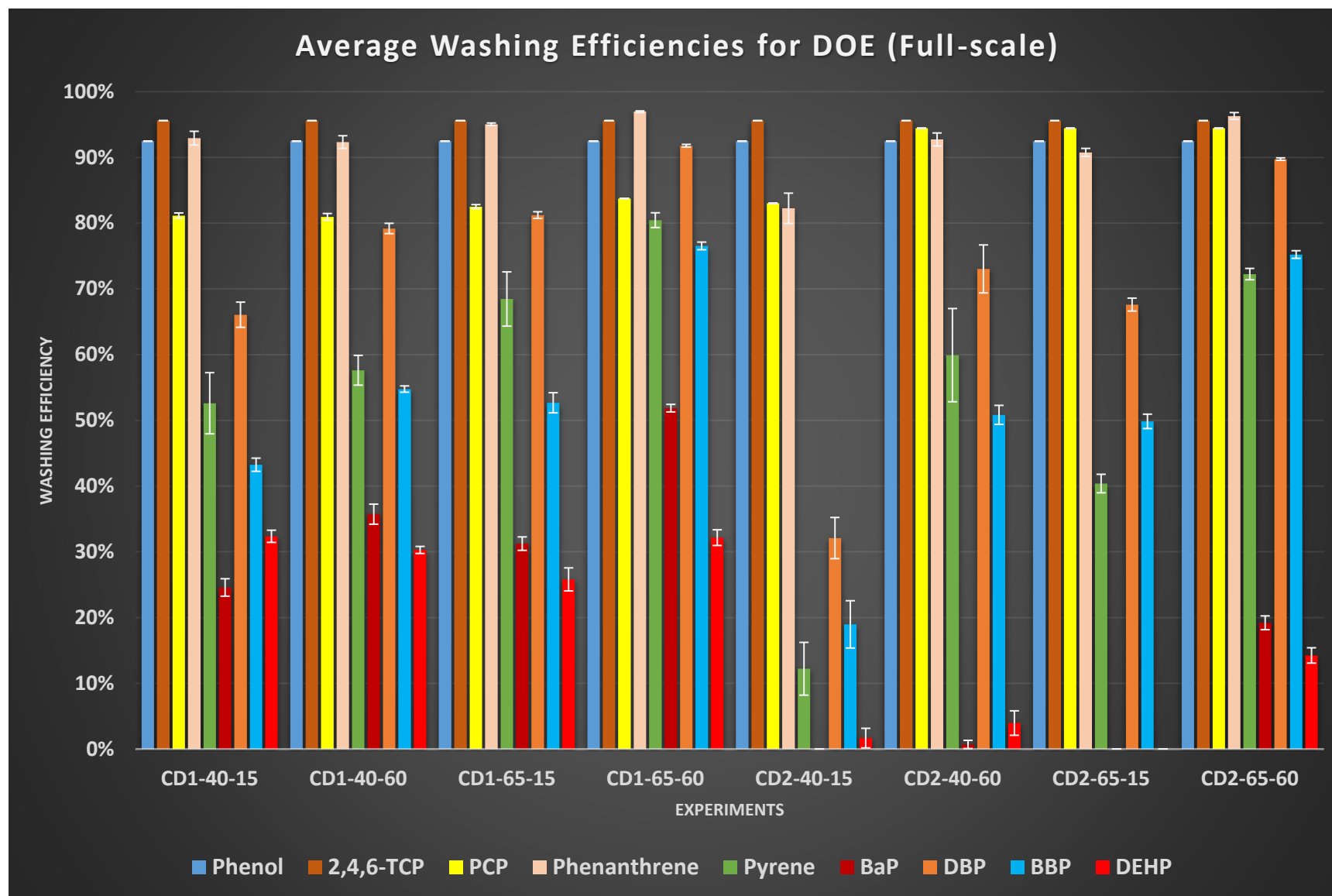


Figure 9-14: Average washing efficiencies for different combinations (Full-scale).

The effect summary of various washing parameters on cleaning efficiency for the entire mix of the targeted contaminants is shown in Figure 9-15. The LogWorth value of surfactant was higher than other parameters. The cross-effect of surfactant with temperature had comparable LogWorth values with time and temperature. Thus, the effect of surfactants on full-scale washing was significant. This was consistent with the bench-scale washing experiments. The effect of time on washing efficiency for full-scale washing increased as evident from its LogWorth value. From the bench-scale washing, the important observation regarding time was its negative impact on washing due to the redeposition of the contaminants such as phthalates. This may have been dramatically increased for a longer washing duration. A detailed explanation can be seen in the subsection. The LogWorth value of parameters in decreasing order was surfactants>temperature>time for PAHs (Figure 9-16) and phthalates (Figure 9-17). The effect summary indicated that parameters such as temperature affected the washing efficiency on full-scale washing differently than the bench-scale washing. The individual effects of these parameters and their cross effects are discussed separately.

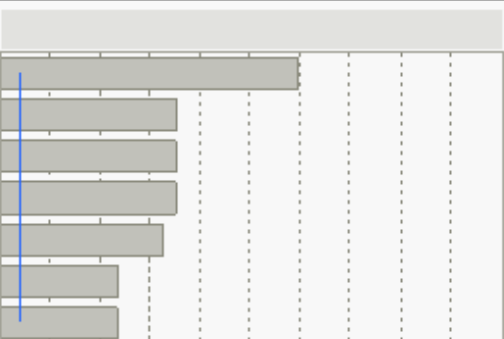
Source	LogWorth		PValue
Surfactants	29.931		0.00000
Time(15,60)	17.794		0.00000
Temperature(40,65)	17.614		0.00000
Surfactants*Temperature	17.614		0.00000
Surfactants*Time	16.366		0.00000
Temperature*Time	11.774		0.00000
Surfactants*Temperature*Time	11.774		0.00000

Figure 9-15: Effect summary for entire mix (Full-scale).

Source	LogWorth		PValue
Surfactants	28.790		0.00000
Time(15,60)	17.224		0.00000
Temperature(40,65)	14.463		0.00000
Temperature*Time	10.079		0.00000
Surfactants*Time	5.260		0.00001
Surfactants*Temperature*Time	2.358		0.00438
Surfactants*Temperature	1.219		0.06045

Figure 9-16: Effect summary for PAHs (Full-scale).

Source	LogWorth		PValue
Surfactants	21.999		0.00000
Time(15,60)	17.794		0.00000
Temperature(40,65)	16.924		0.00000
Surfactants*Time	6.680		0.00000
Temperature*Time	4.850		0.00001
Surfactants*Temperature	4.397		0.00004
Surfactants*Temperature*Time	3.120		0.00076

Figure 9-17: Effect summary for phthalates (Full-scale).

Source	LogWorth		PValue
Surfactants	29.931		0.00000
Temperature(40,65)	17.614		0.00000
Surfactants*Temperature	17.614		0.00000
Time(15,60)	16.366		0.00000
Surfactants*Time	16.366		0.00000
Temperature*Time	11.774		0.00000
Surfactants*Temperature*Time	11.774		0.00000

Figure 9-18: Effect summary for phenols (Full-scale).

### 9.5.2.1 Surfactants

The comparative analysis of prediction profiles for PAHs on both scales is illustrated in Figure 9-19. The surfactant CD1 removed PAHs which is consistent with the bench-scale washing. The difference between bench & full-scale washing is the contaminant to the surfactant volume ratio. For bench-scale, every contaminant is present in the amounts of 60000 ng. In a single flask, the amount of surfactant injected was 45 $\mu$ L. Thus, the ratio was 1333.34 ng of contaminant per  $\mu$ L of surfactant solution. For full-scale, this decreased to 2.5 ng of contaminant was available per  $\mu$ L of surfactant. This increase in the concentration of the surfactants increased the micelle concentration that produced the hydrophobic cavities. Thus, the adsorption of these contaminants from the fabric to these cavities increased as more available sites were available. This helped in the better removal of contaminants. The increase in the G-force increased the mechanical agitation thus helping in the removal of contaminants. A similar trend was observed for phthalates (Figure 9-20) that showed the washing efficiency for CD1 was higher. Compared to the bench-scale, DEHP showed a steep decline for change in surfactant. This indicated that for higher surfactant concentration, hydrophobic phthalates did show little sensitivity to the change in surfactant. The mixed ionic surfactants system in CD2 was not favorable for removing phthalates. Thus, for non-polar compounds, CD1 was better in removing phthalates which were consistent with the bench-scale washing experiments. Although phenol, 2,4,6-TCP was removed in using both surfactants, PCP responded positively for CD2 used for longer washing duration at higher temperature although the results were comparable (Figure 9-21). This may be due to the higher concentration of anionic surfactants that enabled solubilizing the PCP by forming salts with the counterion.

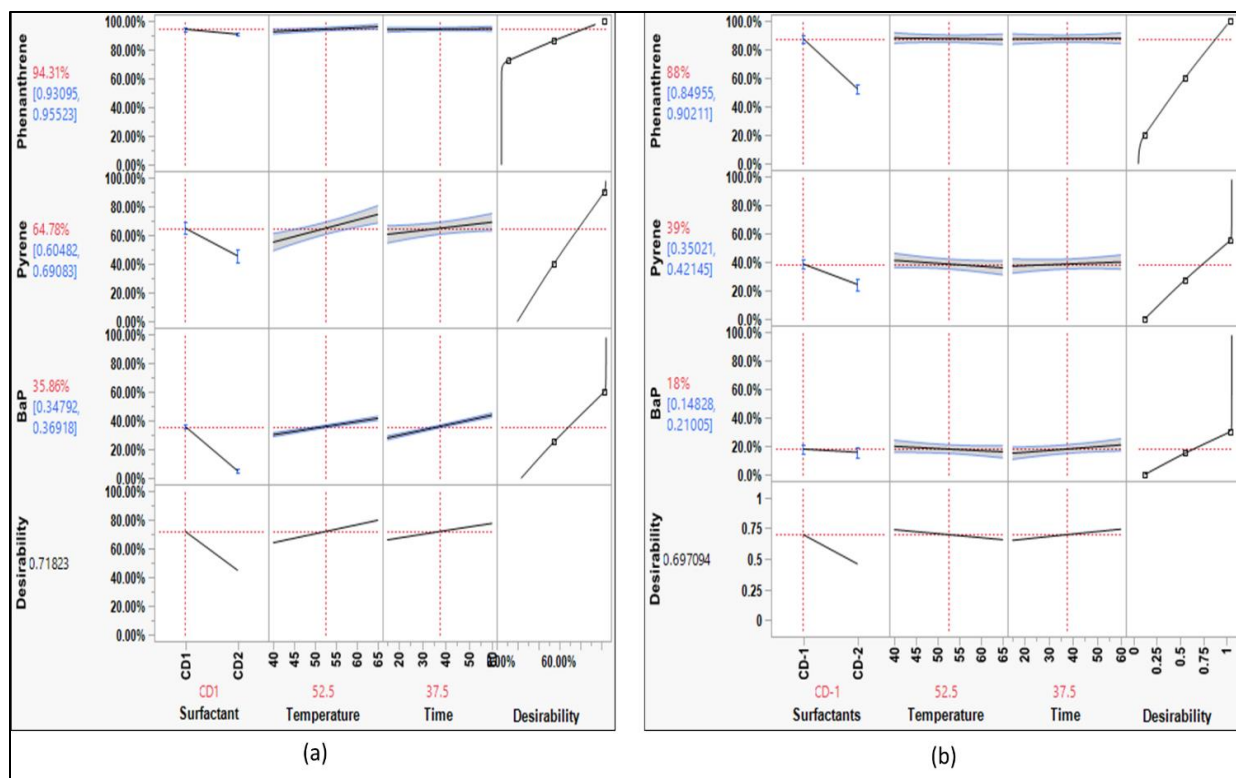


Figure 9-19: Prediction profile for PAHs: (a) Full-scale (b) Bench-scale.

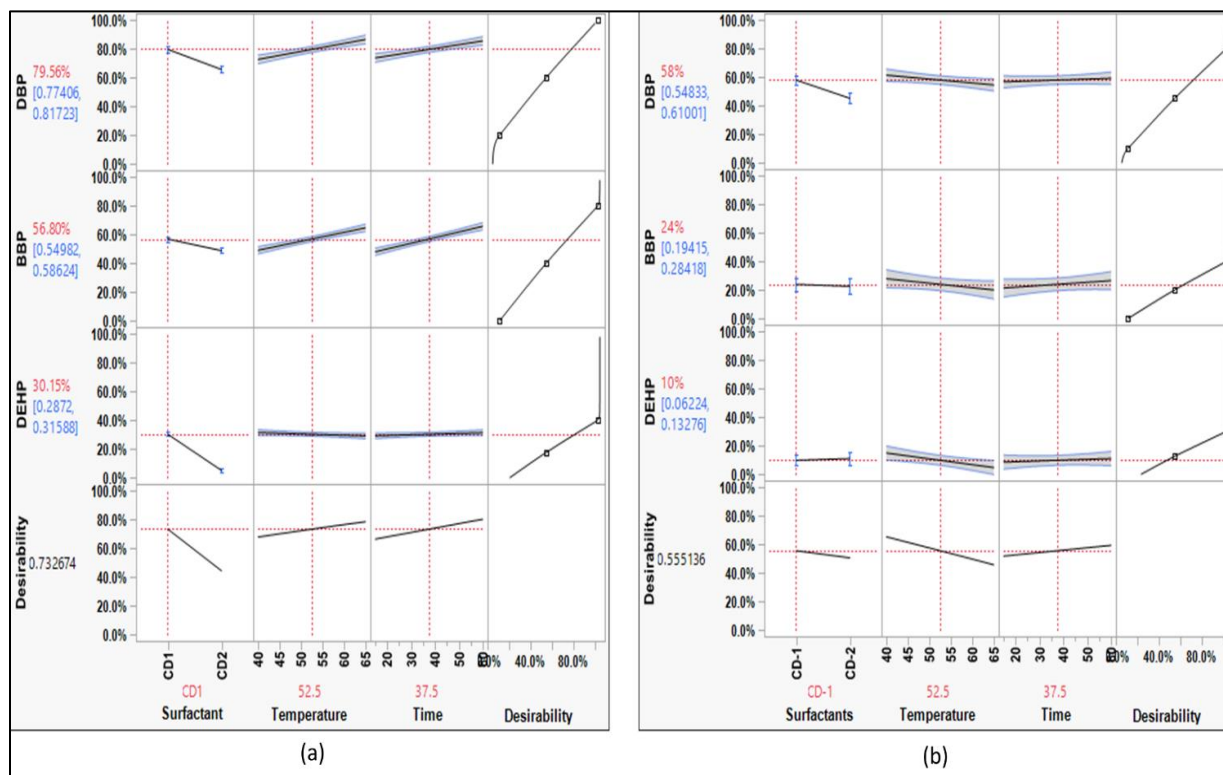


Figure 9-20: Prediction profile for phthalates (a) Full-scale (b) Bench-scale.

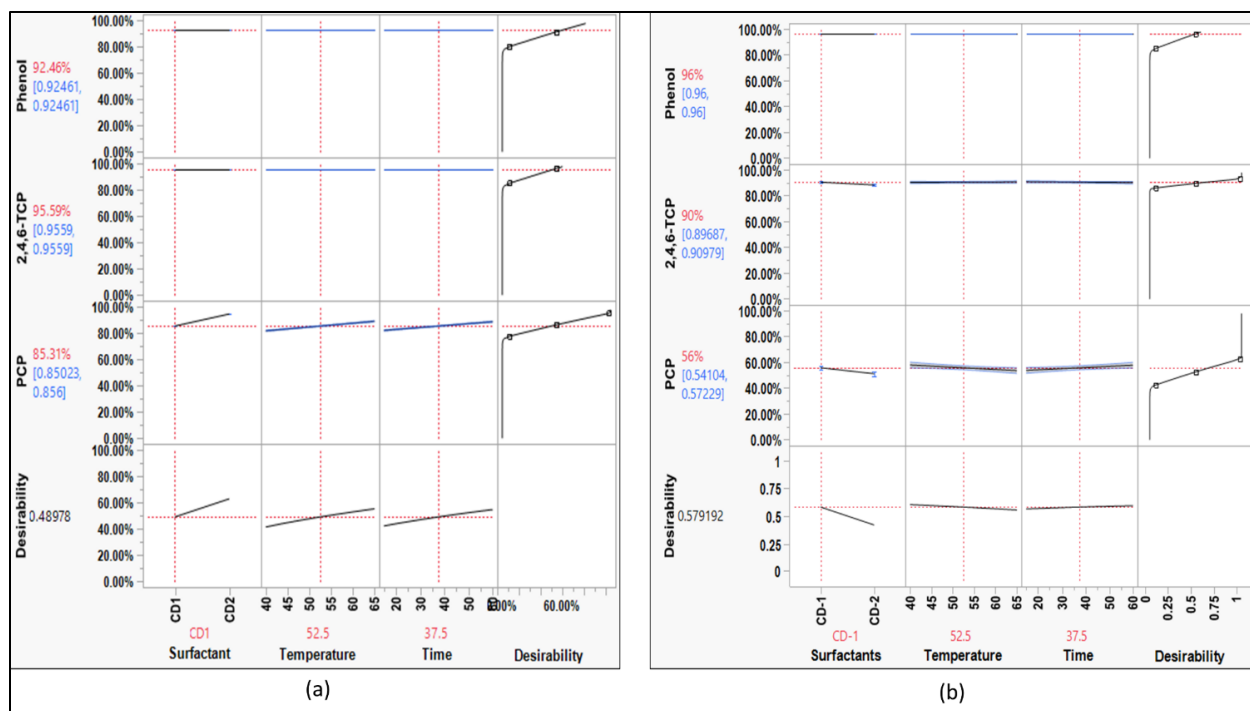


Figure 9-21: Prediction profile for phenols (a) Full-scale (b) Bench-scale.

### 9.5.2.2 Temperature

The effect of temperature on washing efficiency was positive for removing all three classes, unlike bench-scale washing. The primary reason for this was the high concentration of surfactants. The high availability of surfactants molecules for contamination on full-scale contributed to the high removal of contaminants. For full-scale washing, temperature variation was high during the washing cycle that also may have contributed to removing the compounds. Increasing the temperature of the surfactant solution may have reached the temperature close to the cloud point. Non-ionic surfactants have maximum surface activity near the cloud point. This helped in removing the compounds more effectively. The interaction plots for PAHs (Figure 9-22), showed that both the surfactants CD1 and CD2 had a positive effect for increasing the temperature. Similarly, for phthalates (Figure 9-23), especially DBP and BBP, the increase in temperature gradually increased the washing efficiency for surfactants. DEHP in full-scale washing similar to bench-scale washing did not respond to higher temperatures since it is not



partitioned into water easily. This showed that the interaction of surfactants with contaminants is important for hydrophobic compounds and other parameters have a secondary or complementary effect on their removal. The washing efficiency was constant for the surfactant temperature curve for DEHP in interaction plots (Figure 9-23). The effect of temperature on phenols was not significant. This was primarily because the phenols were having strong interaction with surfactants and were removed. The response curve was primarily driven by PCP. An increase in temperature for phenols indicated a slight decline in its removal although the results were comparable. For PCP, there was weak interaction of CD1 with temperature and time (green highlighted boxes) in Figure 9-24.

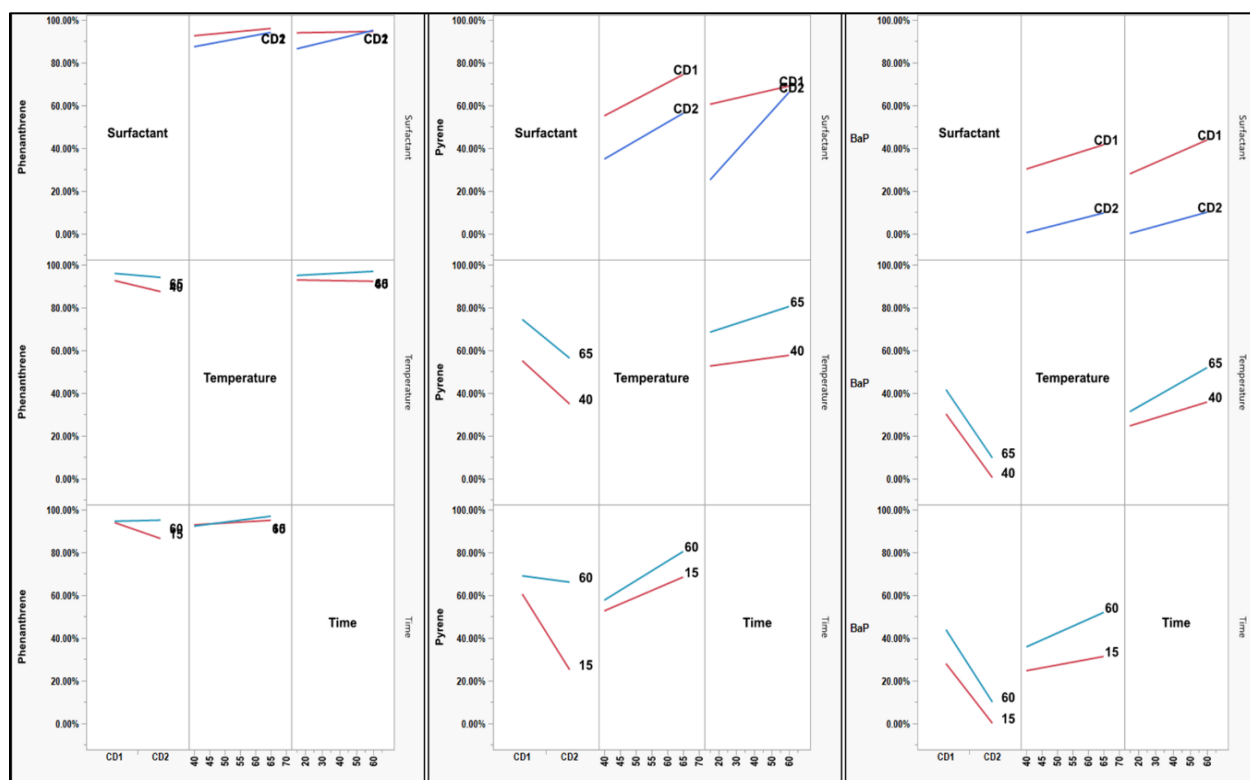


Figure 9-22: Interaction plots for PAHs (Full-scale).

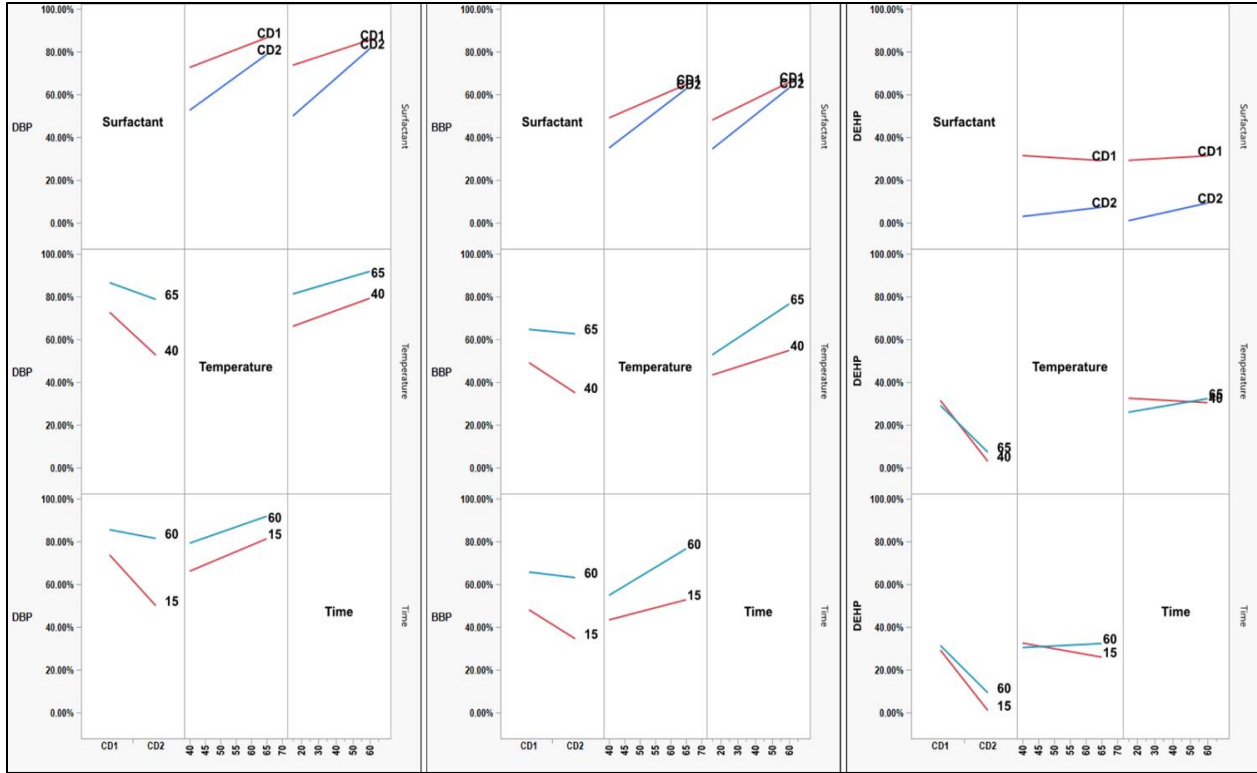


Figure 9-23: Interaction plots for phthalates (Full-scale).

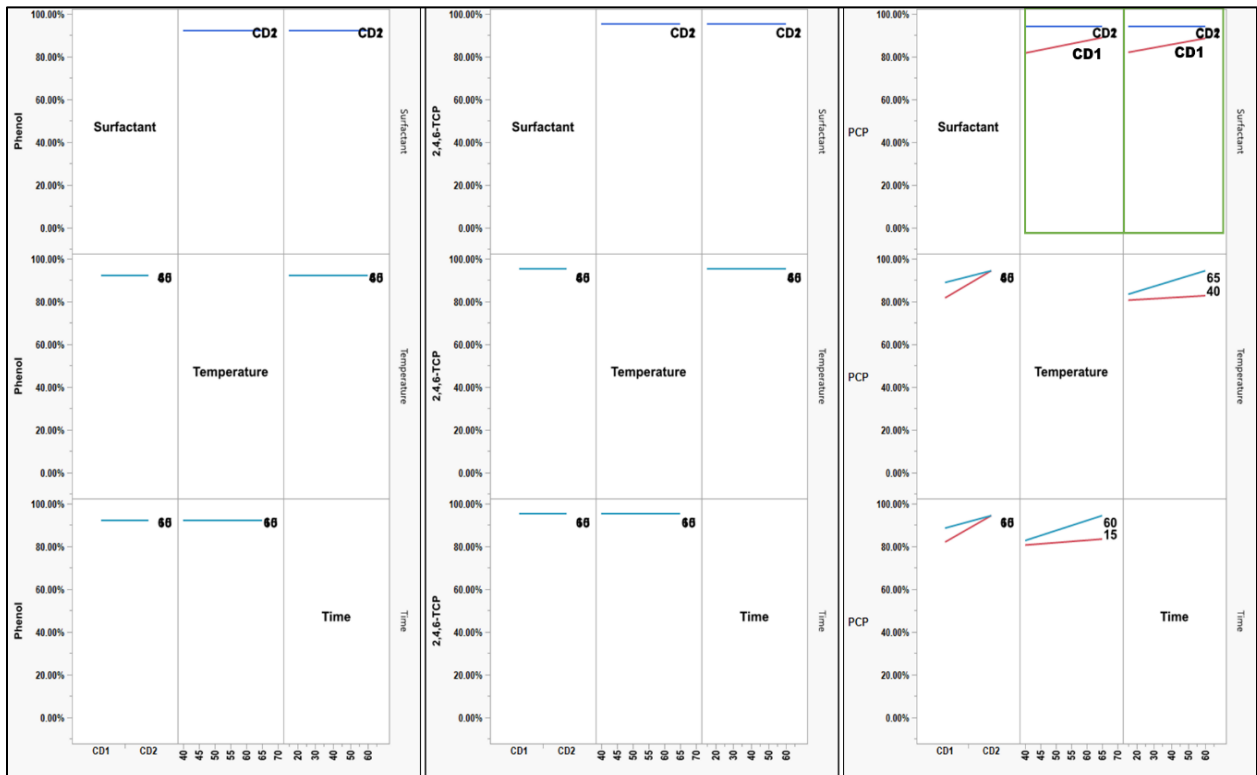


Figure 9-24: Interaction plots for phenols (Full-scale).

### 9.5.2.3 Time

For full-scale washing, the effect of time showed positive results for most of the targeted contaminants. This indicated that when the availability of surfactants molecules is present in higher amount the desorption of contaminants can be driven by time. A significant impact was observed on pyrene and BaP as seen in Figure 9-19. The interaction plots of the PAHs showed that for pyrene, the washing efficiency of the surfactants improved drastically while for BaP it improved gradually. This indicated pyrene and BaP take a longer time to be removed from the fabric. The removal of phthalates was similar to the PAHs. The longer duration of washing improved the removal of DBP and BBP. The interaction plots for time and surfactant in Figure 9-23 indicated that the washing efficiency of surfactants improved gradually for longer washing durations. For DEHP, the surfactant curve was consistent indicating that the current surfactants can remove limited DEHP irrespective of the parameters. For phenols, the effect of time was consistent with the bench-scale washing. The effect was a slight increase in the washing efficiency for CD1 for removing pentachlorophenol. This showed that phenols are washed out at shorter durations when the effect of surfactant was strong. From the bench-scale washing, the possibility of redeposition for the contaminants was seen. There is a possibility that the contaminants might be redeposited on the other parts of the jackets other than swatches thus affecting the calculations.

## 9.6 Conclusion

The primary aim of this study was to evaluate the effects of various washing parameters on the bench-scale level washing method developed and compare the research findings on full-scale washing by simulating the DOE. The results on bench-scale level washing showed that different parameters affect the washing efficiency of different chemicals. The effect summary concluded that all parameters and their cross-effects have an impact on cleaning.

From the three parameters evaluated, the effect of surfactant was significant on cleaning efficiency. The chemistry between the surfactants and targeted contaminants was an important factor that affected washing efficiency. The non-ionic detergent CD1 demonstrated better results for PAHs, phthalates as compared to the CD2. This showed that the non-ionic detergent was better at removing targeted contaminants that had moderate hydrophobicity. There was an inverse relation of  $K_{OW}$  values with washing efficiency. Of all the nine contaminants, removal of BaP and DEHP was very low. Thus, the development of the surfactants will allow for more testing possibilities. The effect of temperature individually on the cleaning efficiency was not significant on the targeted contaminants on the bench-scale level. The interaction plots indicated longer washing duration and higher temperature can improve the washing efficiency for phenanthrene, PCP, BBP. On bench-scale washing, the effect of time worked in both directions. Complex PAHs such as BaP were removed when the surfactant solution was in contact with the fabric for longer washing durations while phthalates such as DBP, BBP were redeposited on the fabric.

Overall, the bench-scale washing simulated the full-scale washing. The prediction profiles for all three classes for surfactants were nearly the same. The effect summary showed surfactant had a significant impact on washing duration on full-scale similar to the bench-scale

washing. Bench-scale washing correctly predicted low removal of BaP, DEHP which was observed in full-scale washing. The primary observations during the full-scale washing experiments were: (1) The temperature variation in the full-scale washer-extractor was high. For 40°C experiments, the temperature reached around 45°C. Similar variation was observed for 65°C experiments, (2) From the data gathered, the washer-extractor used 41 gallons of water for a single experiment. The sheer volume of the surfactant and water contribute to the removal of contaminants. The overall washing efficiency of all the contaminants increased for all the experiments in full-scale washing. The ratio of contaminant per  $\mu\text{L}$  of surfactant was low for full-scale washing. This was one of the reasons for differences in both the results.

The effect summary Figure 9-4 highlighted the cross effects of parameters that affect the removal of contaminants. The parameters 40°C and 60 mins for this DOE were assumed as the conventional wash (wash according to the NFPA 1851 guidelines) and it showed that the contaminants such as BaP, DEHP are not removed effectively. Phenols being polar in nature were removed significantly. Simpler PAHs such as phenanthrene and phthalates such as DBP are removed effectively by conventional wash. As the hydrophobicity of the compound increases, the removal of the contaminants from the fabric is difficult. This was significantly highlighted for phthalates where irrespective of the parameters there was low contaminant removal. The chemistry of phthalates dominated other effects. As the washing duration increased compounds such as TCP, BBP showed a gradual decrease in removal of contaminants that indicated the case of redeposition of the compounds. Also, since the master mix contained the chemicals the interactions between the chemicals need to be considered.

The absence of G-force is a shortcoming on the bench-scale. For future work, a prior calculation on a contaminant to surfactant ratio would help in decreasing the differences in

results for both levels. For the full-scale, the main effect summary showed that the choice of surfactant has a very high impact on the removal of contaminants. The migration of contaminants from swatches to the other parts of the garment may affect the calculation of washing efficiency for the contaminants. This was a major limitation for the full-scale washer-extractor study design. Thus, investigating in the redeposition studies is important. Similar to the bench-scale, the simpler PAHs, phthalates and phenols are removed effectively in the full-scale approach. The conventional detergents have limited potential in removing phthalates such as DEHP and for complex PAHs such as BaP. As such, a synergistic effect of the high temperature and washing duration has potential as concluded from the data model.

The effects summary for different groups of compounds was different for both bench-scale and full-scale levels. Although the removal of contaminants is a complex phenomenon with no one correct solutions certain things can be done till the time better cleaning alternatives are available. Based on the research findings, the use of a non-polar surfactant at 40°C for around 60 minutes would be sufficient to remove phenols, simple PAHs. The limitation of this method would be the low removal of compounds such as BaP, BBP, DEHP. The complex PAHs, phthalates have a stronger affinity towards organic matter such as particulates. In such cases, the on-scene decontamination can be used to remove the maximum particulate contamination to minimize the contamination of stubborn compounds. Also, specialized cleaning methods need to be developed to remove any residual contamination that is not cleaned by regular wash. This would decrease the potential health hazard from such contamination.

## **Chapter 10: Bench-scale Testing of Different Surfactants**

### **10.1 *Introduction***

The bench-scale method was developed at the TPACC facility. The method provided different surfactant manufacturers a means to test their products and conduct research for improving washing efficiency if needed. A bench-scale method helps in evaluating the effect of surfactants on washing efficiency and cross effects of different parameters can be studied if needed. The commercially available surfactants were tested on the bench-scale level in Section 9.2. The primary conclusion from the study was the chemistry of surfactants has a significant effect on cleaning efficiency. It highlighted the limitations of the available surfactants in removing hydrophobic contaminants and phthalates. Thus, modification of surfactants was required to improve cleaning efficiency.

The primary aim of this research was to evaluate surfactants that can be used on the turnout suits to determine the washing efficiency of the surfactants.

### **10.2 *Materials and Methods***

All the samples were prepared and contaminated using the procedure described in the previous chapter. The level of contamination was kept constant: 60000 ng. The surfactants tested were from different categories: microbial surfactant, Ecolabs provided three different surfactants.

#### **10.2.1 *Microbial Surfactant***

The microbial surfactant manufacturer recommended two application methods for the product's use. One method included pre-soaking the garment and the other was washing directly in the washer-extractor with the recommended amount.

#### *10.2.1.1 Pre-soak Method*

Three contaminated swatches and one uncontaminated swatch were pre-soaked at the recommended amount: 2 oz of microbial surfactant per gallon of water for 45 minutes. The tests were conducted on outer shell fabric only. The material used was PBI Max™ Gold. The swatches were contaminated using a repeater pipetted. The level of contamination was 60000 ng per targeted contaminant on a single fabric. For pre-soaking, the recommended dosage was 2 oz/ gallon of water. Accordingly, for pre-soaking, 15.80 mL of surfactant was used for 1000 mL water in a beaker. All the fabrics were pre-soaked for 45 mins of the recommended time. After pre-soaking all the contaminated swatches were washed at 40°C and the duration was 60 minutes with clean water. As per the instructions, no extra surfactant was added during the washing process. All the washed samples were air-dried for 24 hours at room temperature and analyzed according to the method described in Section 8.2.3

#### *10.2.1.2 Washer-Extractor Method*

The following test was performed on bench-scale. The testing was done on outer shell material PBI Max™ Gold (7 oz). Three contaminated swatches of outer shell fabric were used with one uncontaminated swatch as controlled samples. The swatches were contaminated using a repeater pipette. The level of contamination was 60000 ng for each targeted contaminant on each fabric. The recommended amount of the microbial surfactant was 4-8 oz per load, therefore 6 oz of the detergent was used per load in the washer extractor. Since we were experimenting at the bench-scale, the dosage amount was calculated according to the weight of the material used. It was 45 µL of surfactant in approximately 100 mL water. The temperature of the washing was 40°C and the duration was 60 minutes. This helped in making a direct comparison with CD1 that



was tested in Section 9.3. All the washed samples were air-dried for 24 hours at room temperature and analyzed according to the method described in Section 8.2.3.

### 10.2.2 Modified Surfactants

A leading surfactant manufacturer-provided three different surfactants D1, D2, D3. These surfactants were used along with variations in the temperature and washing duration (Table 10-1). The temperatures used were 40°C and 65°C. The washing duration was 15 mins and 65 mins. The JMP Pro 15 was used for DOE and a fit model test was used for analysis. The detergent D1 and D3 had neutral pH and D2 was an alkaline detergent. The recommended dosage for D1, D2, and D3 was 12 oz, 12 oz, and 24 oz, respectively per 32 gallons of water. For the bench-scale, the dosage was calculated accordingly. Every experiment was done in triplicates. The study was conducted on outer shell material PBI Max™ Gold. Each swatch was contaminated using a repeater pipette. The targeted contaminants were presented in the amounts of 60000 ng per contaminant on each swatch. The ingredients for all three detergents are given in Table 10-2

*All the names are generic due to the non-disclosure agreement.*

Table 10-1: Experimental Design for Modified Surfactants.

<b>Temperature</b>	<b>Time</b>	<b>Surfactant</b>
40°C	15 mins	D1
65°C	60 mins	D2
-	-	D3

Table 10-2:Ingredients of Modified Detergents.

<b>D1</b>	<b>D2</b>	<b>D3</b>
Ethoxylated alcohols	Sodium Silicate	Fatty acid ester
2-methyl-polymer with oxirane	Sodium polyacrylate	Oxirane polymers
1-(2-methoxy-2methyl-ethoxy)-2 propanol	glycine, n,n-bis(2-(bis(carboxymethyl)amino) ethyl)-pentasodium	2-(2-Butoxy-ethoxy) ethanol
		Nonionic surfactant

### 10.3 Results and Discussion

#### 10.3.1 Microbial Surfactant

The microbial degradation has been studied on soil washing experiments for PAHs mainly [205] [206]. The microbes produce enzymes that help in digesting the compounds and producing water and carbon dioxide. The values for washing efficiency are displayed in Table 10-3.

Table 10-3:Washing Efficiencies of targeted contaminants.

<b>Compounds</b>		<b>Without Pre-soak</b>	<b>Pre-Soak</b>
Phenols	Phenol	84.83 <sup>†</sup>	84.83 <sup>†</sup>
	2,4,6-tri-chlorophenol (TCP)	84.17 <sup>†</sup>	84.17 <sup>†</sup>
	Penta-chloro-phenol (PCP)	85.17 <sup>†</sup>	85.17 <sup>†</sup>
PAHs	Phenanthrene	58.95	39.89
	Pyrene	18.44	5.43
	Benzo[a]pyrene (BaP)	0.00	0.00
Phthalates	Di-butyl-phthalate (DBP)	26.11	16.74
	Benzyl-butyl-phthalate (BBP)	6.00	0.00
	Di-ethyl-hexyl-phthalate (DEHP)	0.47	0.00

<sup>†</sup>Non-detectable signal – ½ LOQ used for calculation

The comparative results displayed in Figure 10-1 indicated that the overall washing efficiency of the bench-scale washing (without pre-soak) was better than the pre-soak option when compared together. For phenols, the surfactant was effective, and the compounds were not detected in post-washed samples. The microbes successfully degraded phenols. For PAHs, the microbes degraded phenanthrene showing washing efficiency greater than 50%. The surfactant was not effective in degrading phthalates.

The microbes continually germinate, and the population doubles every 20 minutes. For the pre-soaking option, the fabric was in contact with the surfactant solution for 45 minutes and for bench-scale the contact period was 60 mins. The difference of 15 minutes may be the primary reason for the bench-scale washing to work better. For PAHs, low molecular weight PAHs such as phenanthrene are easily metabolized by microbes. Compared to other PAHs, phenanthrene is more susceptible to microbial attack and has more solubility in water [207]. Complex compounds such as BaP and pyrene have low solubility in polar phases such as water. BaP has a high boiling point hence it is not easy to remove it at lower temperatures and low concentrations.

When results are compared with commercial detergent CD1 from Section 1449.3 in Figure 10-2. It showed that the microbial surfactant did not have any significant advantage over CD1 while removing targeted contaminants. The DEHP is a ubiquitous compound and is difficult to remove in all detergents. Adding a non-polar phase in the detergent may help in improving the washing efficiency of phthalates. The microbial strain that is present in the current surfactant if it can sustain higher temperature might help in removing these compounds more effectively.

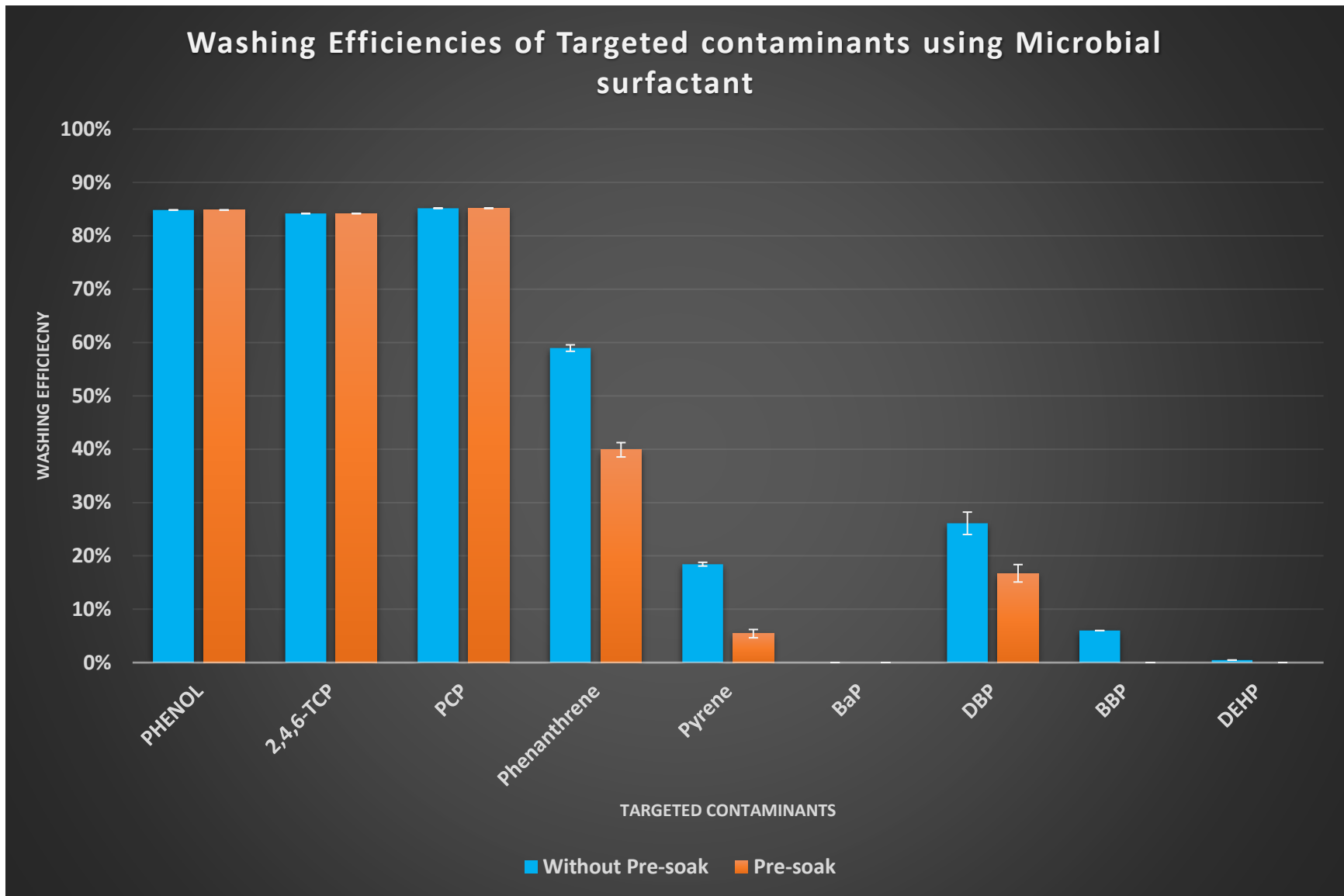


Figure 10-1: Comparative analysis of with and without pre-soak options.

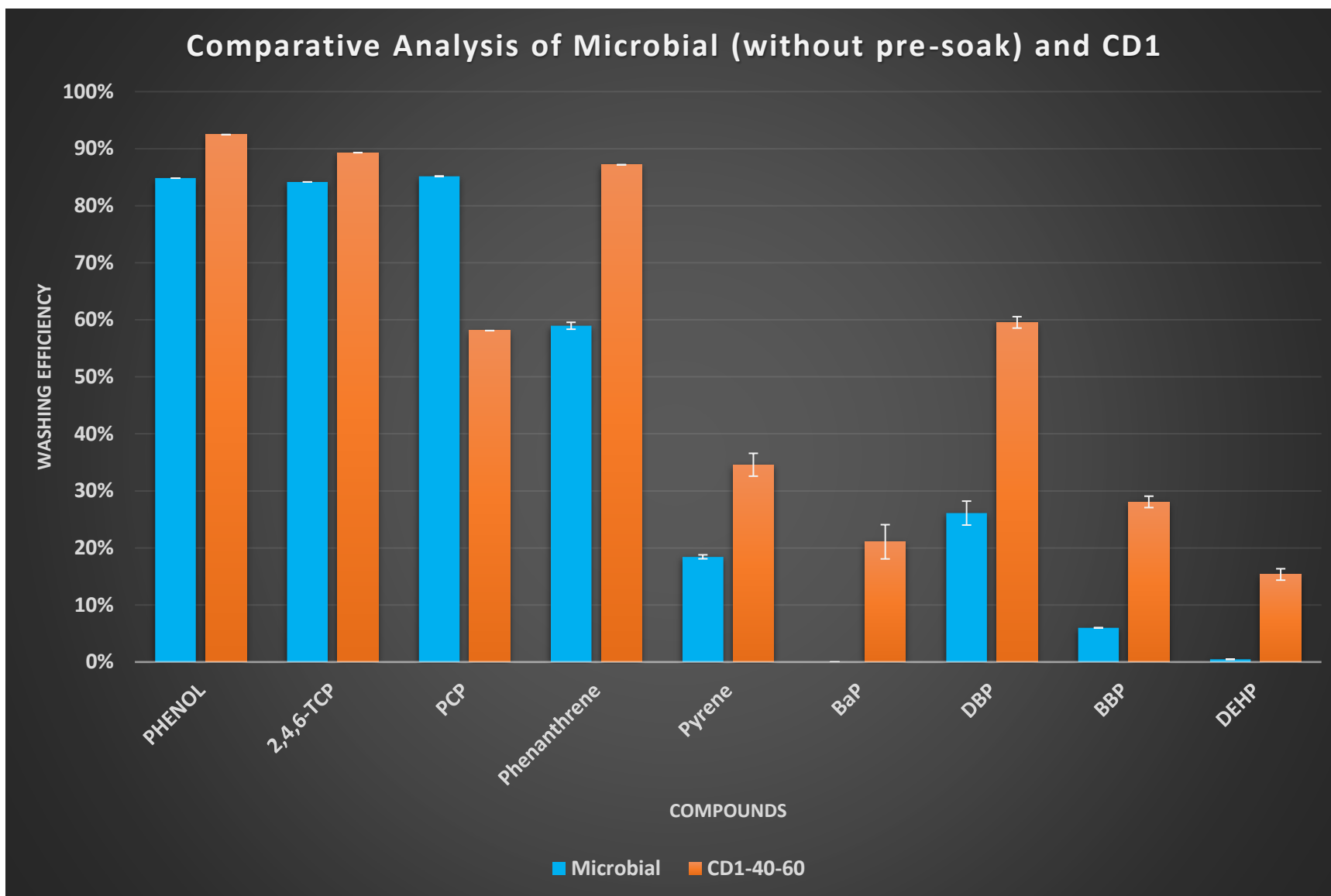


Figure 10-2: Comparative analysis of microbial surfactant with a commercial detergent.

### 10.3.2 Modified Surfactants Testing

The average washing efficiency for modified detergents for phenols is shown in Figure 10-3. The washing efficiencies for phenols were calculated using LOQ/2 values. This meant that the phenols were removed from the fabric beyond the detection limits of the analytical method.

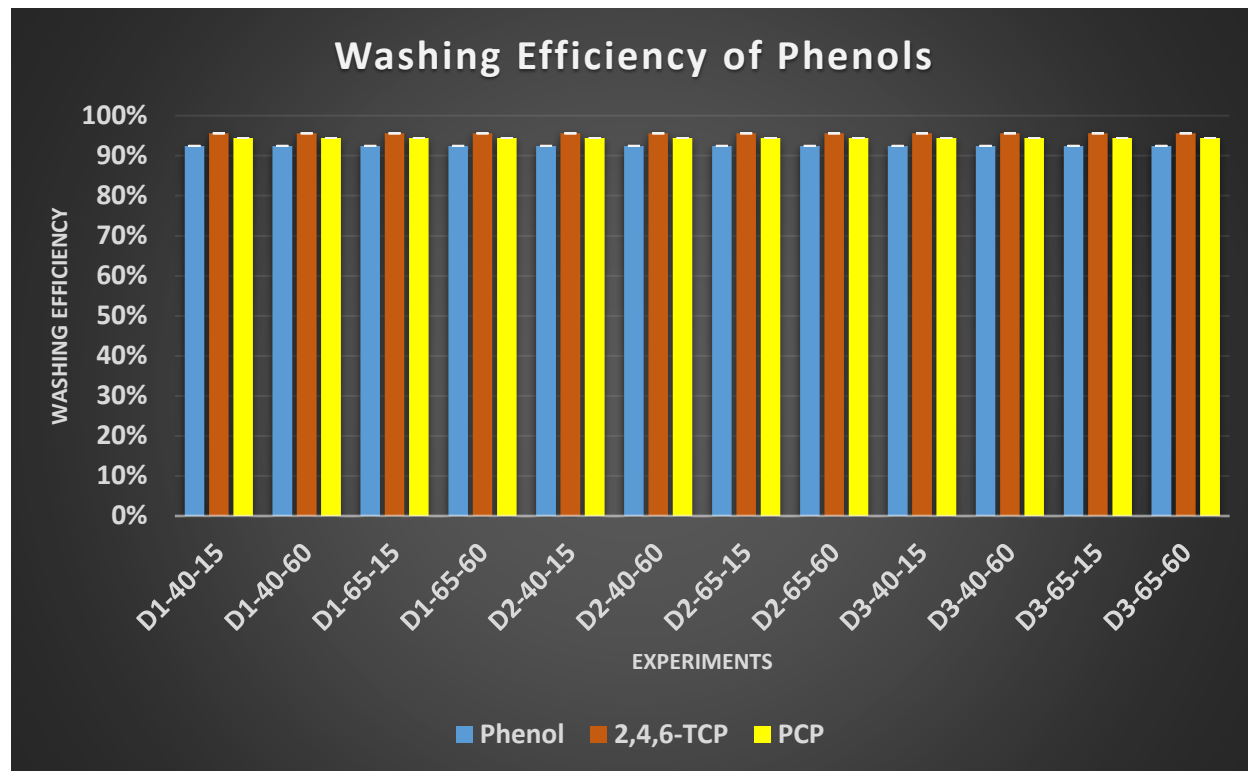


Figure 10-3: Washing efficiency of Phenols.

Figure 10-4 illustrated the average washing efficiencies of modified surfactants for PAHs. All the surfactants removed more than 90% of phenanthrene for all combinations. The surfactants D1 and D3 removed pyrene effectively as compared to D2. The combination of D3-65°C-60 mins was effective in removing more than 80% BaP that showed a significant advantage over the commercial detergents used in Section 9.3.

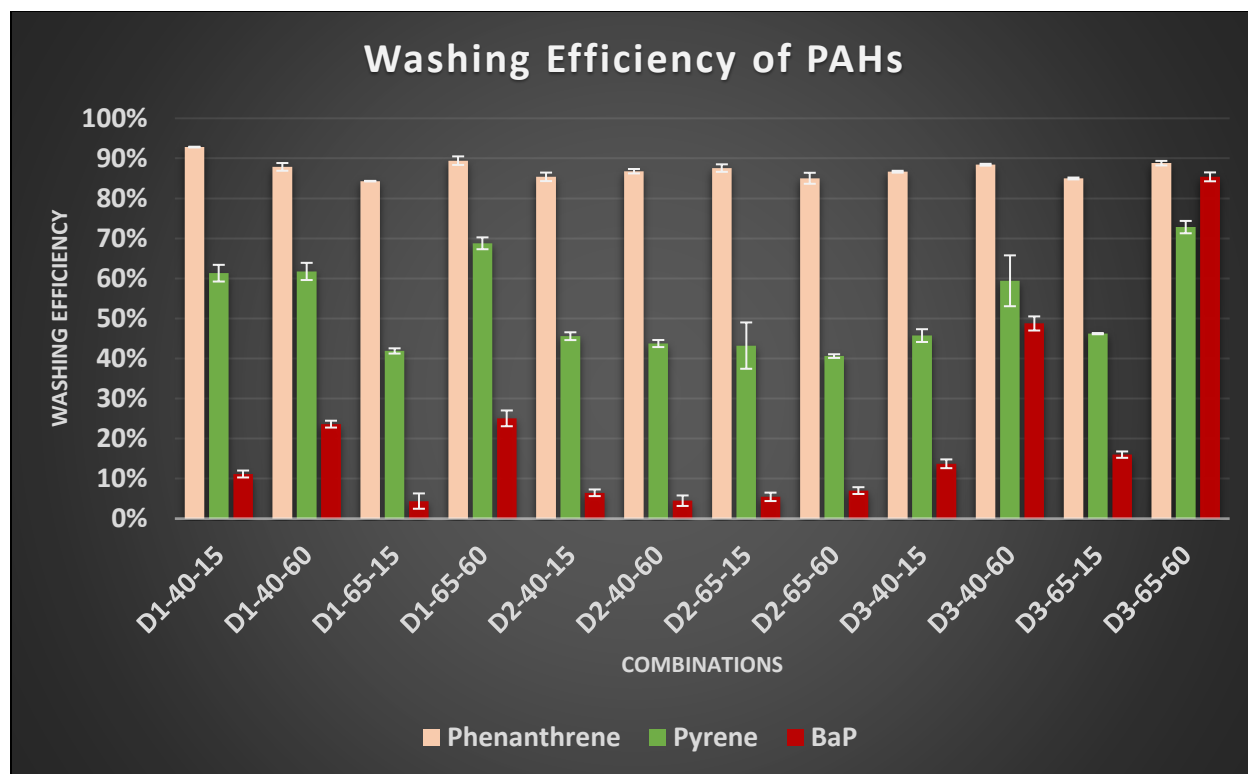


Figure 10-4: Washing efficiency of PAHs.

Similar to the PAHs, the average washing efficiency of the surfactants was high for phthalates as shown in Figure 10-5. For DBP the average washing efficiency was greater than 60% for all surfactants. Surfactants D1 and D3 removed BBP by more than 50% for longer washing durations. Although the washing efficiency of DEHP was low amongst all the contaminants it was comparatively high when the results from Section 9.5.1 were compared.

Thus, the modification of surfactants certainly improved the average washing efficiencies of targeted contaminants. The inverse relation of washing efficiency with  $K_{OW}$  value was consistent with the results seen in Section 9.3

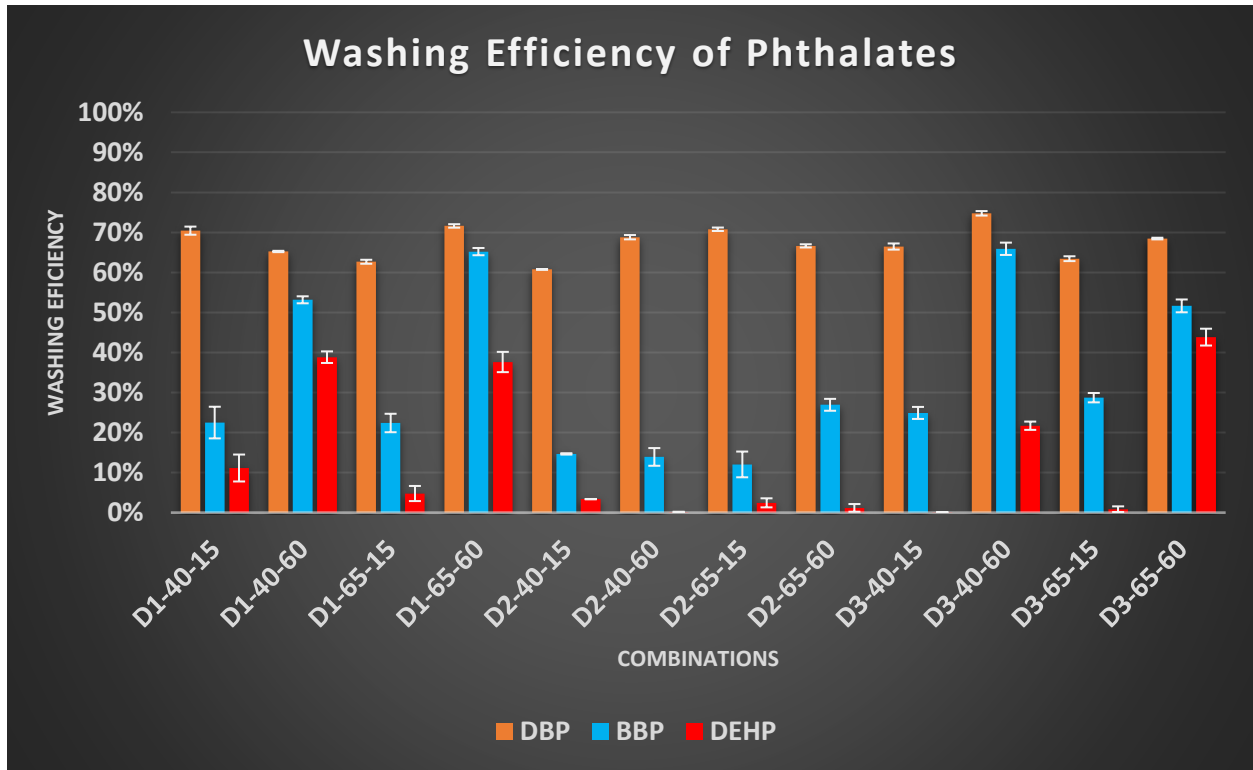


Figure 10-5:Washing efficiency of phthalates.

The effect summary for the experiment is shown in Figure 10-6. The surfactants and time along with the cross effect of time and surfactant together demonstrated a high LogWorth value. This indicated that the surfactant contact time with the fabric was a crucial parameter in removing the contaminants effectively.

Source	LogWorth	PValue
Surfactants	18.986	0.00000
Time (mins)(15,60)	17.294	0.00000
Time (mins)*Surfactants	16.075	0.00000
Temperature(degree C)*Surfactants	8.867	0.00000
Temperature(degree C)*Time (mins)	7.616	0.00000
Temperature(degree C)*Surfactants*Time (mins)	6.019	0.00000
Temperature(degree C)(40,65)	5.696	0.00000 ^

Figure 10-6:Effect Summary for Modified Detergents.



Another important point for this study was the recommended amount for the detergents was higher as compared to the commercial detergents that were used in the previous chapter. The recommended amount in 100 mL water for D1, D2 and D3 were 300  $\mu\text{L}$ , 300  $\mu\text{L}$  and 600  $\mu\text{L}$ , respectively. The contamination on one single swatch for a single compound was 60000 ng. The ratio of contaminant to surfactant was D1:200 ng/  $\mu\text{L}$ , D2:200 ng/  $\mu\text{L}$ , D3:100 ng/  $\mu\text{L}$  which was high compared to CD1 and CD2 which was 1333.34 used in Section 9.3. This may have been a primary reason for the high washing efficiency. Phenols are removed in higher amounts for all the combinations of the detergents as shown in Figure 10-3. The low  $K_{\text{OW}}$  values and the polar nature of phenols help in removing these contaminants from the fabric surface effectively. All the values were calculated using LOQ/2 values. Thus, phenols were washed out beyond the detection limits of the analytical method developed. The hydrophobic compounds can be desorbed by being partitioned into the hydrophobic cores of surfactant micelles above their critical desorption concentration that depends on the critical micelle concentration [201], [202]. Thus, the complex PAHs such as BaP and phthalates such as BBP and DEHP were removed effectively using D3. The average washing efficiencies for PAHs for all combinations are shown in Figure 10-4. The combination of D3-65°C-60 mins removed all the PAHs effectively as compared to the other combinations. This was in conjunction with the effect summary results that a longer period of contact of fabric with a detergent solution was effective in removing contaminants from the fabric surface. A similar trend can be observed for phthalates. As the hydrophobic nature of the compounds increased in the order: DBP<BBP<DEHP the removal of these compounds decreased. DBP was removed in significant amounts for all the combinations. The combination of D3-65°C-60 mins removed more than 40% DEHP. It has been shown that for surfactants such as alcohol ethoxylates, the longer alkyl chain solubilizes in water decreasing

the surface tension values. For nonionic surfactants, when the surfactants are present in high concentration, the adsorption of hydrophobic tails of the surfactant on the hydrophobic surface increased improving the removal of contaminants [110]. Also, the synergistic effects of fatty acid ester and nonionic surfactants have been shown to remove contaminants effectively [208].

#### 10.4 *Conclusion*

The bench-scale level washing enabled helped in the evaluation of different surfactants and can be used in screening surfactants and plotting their interaction with different washing parameters. The microbial surfactant used in the study when compared with the commercial surfactant did not provide any distinctive advantage. The microbes in the surfactant worked better in removing phenols and phenanthrene. These microbes in the detergent consume the compounds for energy and produce water and CO<sub>2</sub> as byproducts. This is a very sustainable approach to decontamination. The testing of the detergent provided a concept of microbial decontamination of the turnout suits. The incorporation of contaminant-specific microbes can help in removing hydrophobic contamination such as BaP and DEHP that are difficult to remove using conventional detergents.

The modified detergents provided by a manufacturer showed promising results in the removal of targeted contaminants. The effect summary demonstrated that the choice of detergent has a significant impact on removing the contaminants. The measurably high concentration of the detergent improved the removal of contaminants from the fabric. The highlighted part of the study was the high removal of hydrophobic compounds such as BaP and DEHP when compared with the previous testing of detergents. The combination of high temperature and longer washing duration for detergent D3 worked effectively. This combination was selected for further

investigation in this research on the retired turnout suits and subsequently, its impact on the durability of the turnout suits was studied.

## **Chapter 11:Comparative analysis of the liquid CO<sub>2</sub> washing with conventional wash**

*Sections of the following chapter were submitted for the AATCC paper competition 2021*

The International Agency for Research on Cancer (IARC) has stated the firefighting profession as possibly carcinogenic to human beings [209]. Firefighters are exposed to several chemicals during fire suppression activities. Polycyclic aromatic hydrocarbons (PAHs) are compounds that are released due to the incomplete combustion of materials. PAHs have toxic and mutagenic properties while some of them are endocrine disruptors. Benzo[a]pyrene is a known carcinogen that was found in French firefighters' PPE [34]. Among several different compounds, plasticizers are also found on PPE. When used samples were analyzed 20 different PAHs and 6 phthalate esters were found. Phthalates are ubiquitously found in polyvinyl plastic materials that are used abundantly in flooring, wire sheathing, furnishing [210].

The NFPA 1851 standard on selection, care, and maintenance has standard guidelines for cleaning and maintaining the firefighter turnout gear. These guidelines include washing at temperatures less than 105°F (40°C), G-forces should be less than 100 G, and prohibiting the use of bleaching or oxidizing agents. The standard has categorized the decontamination techniques as (1) Preliminary exposure reduction, (2) Advanced cleaning, (3) Specialized cleaning. The advanced cleaning procedure permits the use of programmable washing machines and detergents. The specialized cleaning is performed by a verified service provider. The standard clearly states to use specialized cleaning when the ensemble is inadequately cleaned by advanced cleaning [188].

A limited number of studies have been conducted that indicate residual contamination after using the standard aqueous wash. Fent et al. investigated the impact of routine laundering

on firefighter hoods and showed that routine laundering helps remove the contaminants. The study was performed on two sets of hoods that were exposed to the same structural fire. One set was routinely laundered after every fire scenario and in total was washed four times in a standard washer extractor. The other set was kept unlaundered to assess the contamination. The analysis between the two sets showed that overall laundered hoods had 81% lower PAH contamination than unlaundered hoods. The pre-wash and post-wash analysis were performed on completely different sets of hoods. The high values of standard deviation in contamination indicated high spatial variability that may have affected washing efficiency results [9]. The study of water-only decontamination on a turnout gear used in live structure burn showed an increase in contamination by 42%, however, this increase could have been attributed to the disparity in sampling sites for pre- & post-washing samples [10]. Thus, the uneven contamination on the gear is a major hindrance in calculating the washing efficiency of the method and prevents from gaining a comprehensive understanding of the process. All the above studies indicated a need for a controlled study that includes uniform contamination and targeted contaminants.

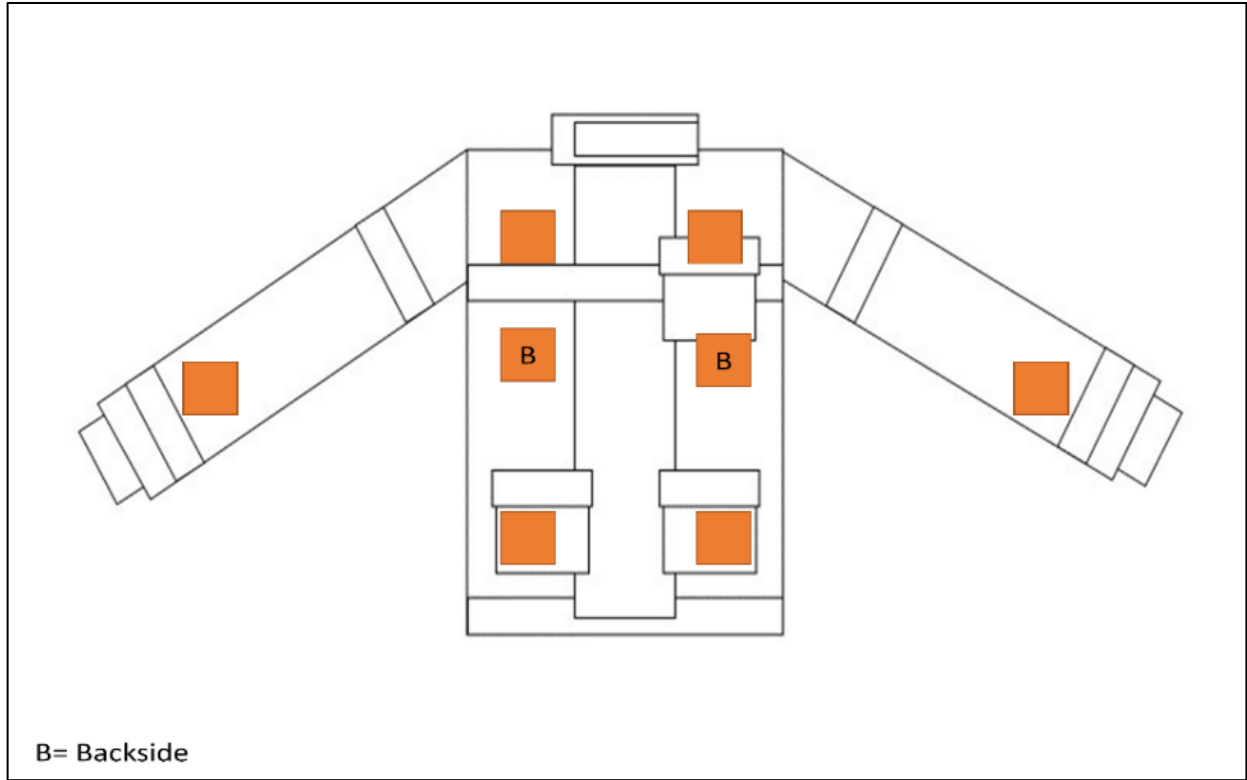
Dry cleaning is a technique of removing soils and contaminants from textiles using a non-aqueous solvent. In conventional dry cleaning, perchloroethylene (PER) is most commonly used. PER has a toxic effect on the human body. Research studies have demonstrated that PER exposure by inhalation and ingestion can damage the liver, kidneys and can cause cancer in animals as well as humans [163]. Several alternatives have been looked for textile dry cleaning applications such as hydrocarbon solvents, Green earth®, acetal silicon-based solvents, and carbon dioxide (CO<sub>2</sub>) [211]. CO<sub>2</sub> has several advantages over other solvents such as being non-toxic, non-flammable, non-corrosive, environmentally benign, economical [163]. Some of the studies have indicated that the cleaning efficiency of CO<sub>2</sub> for non-particulate soil removal is

comparable to that of PER. The particulate removal for CO<sub>2</sub> dry cleaning was lower [163]. For dry cleaning operations, the liquid state of CO<sub>2</sub> is preferred over the supercritical state since the two-phase gas-liquid interface is beneficial for trapping soil particles. The substantially higher pressure in CO<sub>2</sub> cleaning makes it easy to separate the CO<sub>2</sub> from the detergent formulation and the soil post-cleaning process. Also, the spontaneous evaporation of CO<sub>2</sub> from the fabric during depressurization saves the energy of drying [139].

The following study was conducted to evaluate and compare the cleaning efficacies of the liquid CO<sub>2</sub> washing and conventional aqueous wash for the application of firefighter protective clothing.

### 11.1 *Materials and Methods*

For this study, five new turnout jackets were used to mount the test samples for cleaning. On every single jacket, eight hook-and-loop patches were stitched. The hook part was stitched on the jacket and the loop part was stitched to the test samples. The position of the patches is shown in the schematic Figure 11-1. The size of the patch was 5 cm x 5 cm. The test sample swatches (5 cm x 5 cm) were prepared separately using the outer shell material, PBI Max™ Gold with a durable water-repellant finish. The swatches were contaminated with targeted fireground contaminants in a manner fashion to Subsection 9.4.1. Three analytical standards for phenols, PAHs, and phthalates (2,000 ng/μL for each component) were used to contaminate the samples. The solutions were diluted to 1,000 ng/μL using n-hexane. Twenty 3-μL drops of each standard mix were applied on the swatch from the stock solution using a repeater pipette. Thus, the amount of each contaminant present on a single swatch was 60,000 ng. All the samples were allowed to dry for 24 hours. After contamination, the swatches adhered to the locations on the turnout jackets.



*Figure 11-1:*Schematic of the turnout suit.

### *11.1.1 Liquid CO<sub>2</sub> Protocol*

To conduct the liquid CO<sub>2</sub> cleaning of the test samples, the research team employed Tersus Solutions (Denver, CO). All of the test jackets were shipped to the cleaning facility to be washed with liquid CO<sub>2</sub> utilizing a protocol that is proprietary to the facility. The limited details of the method are given in Table 11-1.

Table 11-1: Details of the liquid CO<sub>2</sub> method.

<b>Step</b>	<b>Details</b>
Duration of cycle	50 minutes
Wash bath: Single wash	8 minutes
Rinse: Two cycles	4 minutes each
Pressure range	600-850 psi
Total load	50 lbs.
Detergent	Proprietary
CO <sub>2</sub> grade	Beverage

After washing, all the samples were sent back for analysis. The analysis was done using the analytical method described in Section 8.2.3.

#### *11.1.2 Conventional Washing Protocol*

For comparative analysis, the sample preparation process was repeated exactly for the samples to receive conventional aqueous wash using a commercially-available detergent (CD-1). The ingredients of CD1 are shown in Table 9-2. The UNIMAC® 45 lbs. washing extractor was used in this process. The temperature of the wash was kept at 40° C (105° F) and the duration of the wash was 60 minutes. Due to the limited availability of the materials, every jacket was stitched with 5 contaminated swatches. The amount of detergent used was 120 mL in the process and was calculated according to the recommendation. All the samples were air-dried after wash for 24 hours and then extracted and analyzed with the same method.



## 11.2 Results and Discussion

### 11.2.1 Washing efficiency

Following the analysis, the washing efficiency was calculated for both the liquid CO<sub>2</sub> and conventional cleaning processes using Equation 8-2. The original target concentration applied to the materials (accounting for analytical sample preparation) for all the samples was 6 ng/μL. The liquid CO<sub>2</sub> values presented in Table 11-2 for the targeted contaminants are an average of 40 samples. For conventional wash, the average of 5 samples was calculated. The average washing efficiency for conventional wash is shown in Figure 11-2. The comparative analysis of the washing efficiencies is shown in Figure 11-3. The t-test for unequal variances was used to compare the results. The difference was statistically significant for p<0.05. Thus, we reject our null hypothesis and conclude that liquid CO<sub>2</sub> wash was more effective.

Table 11-2: Average washing efficiency of targeted contaminants for conventional and liquid CO<sub>2</sub>.

Compounds		Conventional wash	Liquid CO <sub>2</sub>
Phenols	Phenol	92.46% <sup>†</sup>	92.46% <sup>†</sup>
	2,4,6-tri-chlorophenol (TCP)	95.59% <sup>†</sup>	95.59% <sup>†</sup>
	Penta-chloro-phenol (PCP)	80.96%	94.43% <sup>†</sup>
PAHs	Phenanthrene	92.32%	94.44% <sup>†</sup>
	Pyrene	57.62%	98.22% <sup>†</sup>
	Benzo[a]pyrene (BaP)	35.73%	98.52% <sup>†</sup>
Phthalates	Di-butyl-phthalate (DBP)	79.19%	97.80% <sup>†</sup>
	Benzyl-butyl-phthalate (BBP)	54.76%	97.08%
	Di-ethyl-hexyl-phthalate (DEHP)	30.29%	89.67%

<sup>†</sup>Non-detectable signal – ½ LOQ used for calculation

For conventional wash, the washing efficiency decreased from phenols to phthalates. The increase in the K<sub>OW</sub> values and the decrease in the washing efficiency in a chemical class

showed that the relation between the two was evident. The LOQ/2 values were used for calculating phenol and TCP. The conventional wash removed these contaminants well beyond the detection limits of the analytical method. The aqueous wash and non-ionic surfactants removed the phenols, phenanthrene and DBP. Phenols are more polar as compared to the other two groups. They are fairly soluble in water; hence, the results were comparable. The detergent contained d-limonene for aqueous washing that is a non-polar compound that helped in removing the phenanthrene and DBP. For PAHs, an increase in benzene ring increased hydrophobicity that decreased the removal of the PAHs from the fabric, thus, a decreasing trend in washing efficiency can be seen in the aqueous washing [44]. A similar trend was observed in phthalates, an increase in alkyl chain length increased the hydrophobicity and thus phthalates were not removed effectively by aqueous washing [76].



Figure 11-2: Washing efficiency of the conventional wash.

From the comparative analysis perspective, Figure 11-3 demonstrated that conventional wash was not effective for complex PAHs and phthalates. As seen in Subsection 9.5.2 using the conventional surfactants the aqueous wash was at limitation in removing phthalates and complex PAHs.

For liquid CO<sub>2</sub>, the LOQ/2 values were used in calculations for all the compounds except for BBP and DEHP. It indicated that the contaminants might be present in trace amounts after washing that cannot be quantified by the analytical method. Even for BBP and DEHP, the average washing efficiency was greater than 90%.

The results indicated the potency of the liquid CO<sub>2</sub> method in removing the contaminants. The three different chemical groups: phenols, PAHs, phthalates were all removed effectively using the liquid CO<sub>2</sub> washing method. This may be due to the non-polar nature of liquid CO<sub>2</sub> that helped in hydrophobic contaminants such as phthalates and PAHs. The proprietary detergent used has been effective in removing phenols. The high diffusivity and low viscosity helped liquid CO<sub>2</sub> in reaching the interstices of the fabric and remove contamination. The washing system was kept under high pressure that helped in solubilizing the contaminants from the solvent at low temperature. This made it a very suitable solvent for removing non-polar contamination.

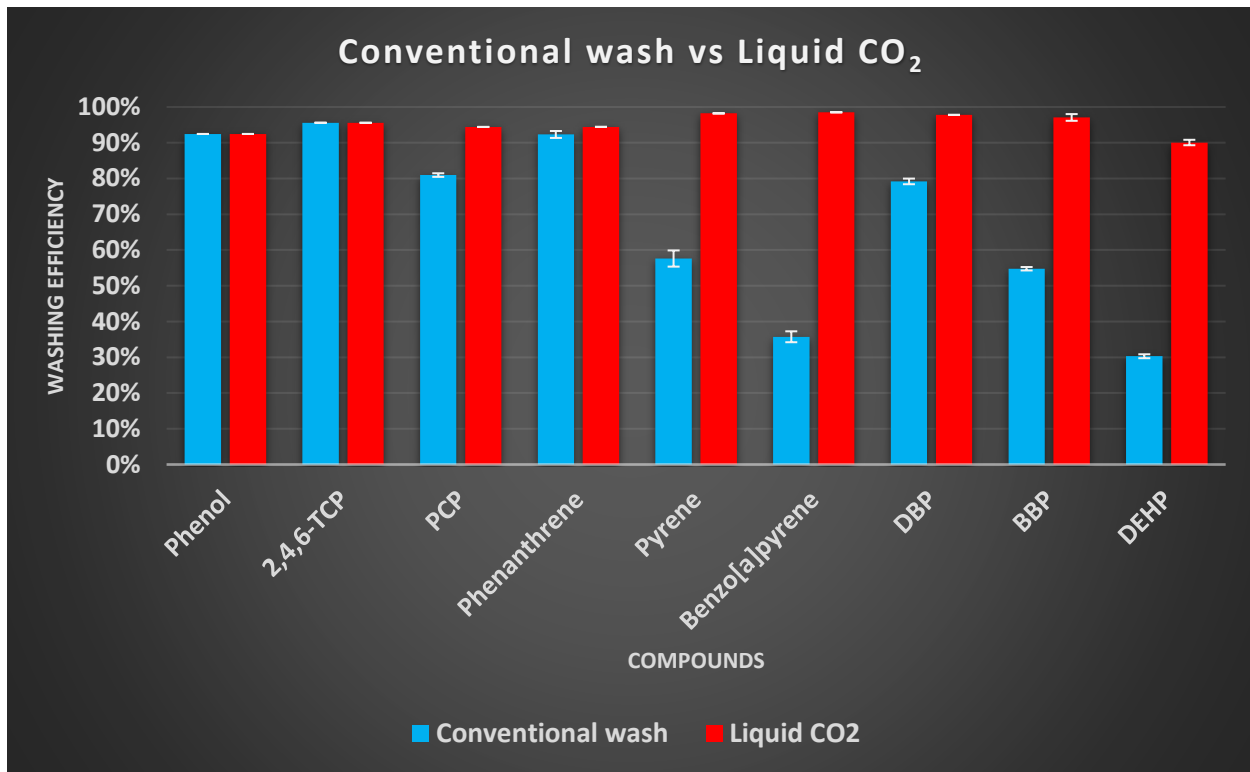


Figure 11-3: Comparison of washing efficiencies for conventional wash and liquid CO<sub>2</sub>.

### 11.3 Conclusion

The liquid CO<sub>2</sub> wash was certainly effective in removing the targeted contaminants. The controlled study included uniform contamination of the garments that helped in understanding and comparative analysis of both methods. The results were statistically significant. The important point to remember is that the method was tested against liquid contamination and did not account for the particulate contamination seen with firefighter exposures. Also, studies have shown that the lack of mechanical action impedes the removal of particulate contamination for liquid CO<sub>2</sub> [163]. Thus, it will be interesting to evaluate the efficacy of liquid CO<sub>2</sub> when real-world samples are used. Simultaneously, it is important to investigate the redeposition of the contaminants while washing with this technique. Also, a further investigation of the impact of liquid CO<sub>2</sub> on the durability of the turnout suit and its accessories is needed.

## Chapter 12: Comparative Analysis of Different Washing Methods on Legacy Gear

*Excerpts from the following chapter were part of the AATCC conference 2020*

### 12.1 **Introduction**

Firefighters are exposed to a high range of chemicals such as semi-volatile organic compounds (SVOCs). The SVOCs include PAHs, phthalates, etc. [6],[8],[38]. The contamination was in particulate form. Post-fire suppression, the turnout suits are contaminated with these residues from the fire [212]. Such contaminated clothing can be a major threat to firefighters' health due to prolonged exposure.

The literature available on cleaning showed the results in the effectiveness of cleaning have huge variation. The decontamination studies indicated a reduction in SVOCs after laundering the ensembles. The on-site decontamination procedures on firefighters' jackets using soap and water reduced PAH concentration by 85%. The simple dry brush technique reduced the PAHs concentration by 23%. [11]. The water-only decontamination subjected to a turnout suit showed an increase in PAHs concentration by 42%. The increase in the results was due to disparity in pre & post-sampling sampling locations on the jacket. [10]. The study on decontamination of the outer shell swatches patched on the outside of the PPE that was exposed found a 44% increase in the BaP concentration [34]. Most of these studies used wipes to collect the contaminants from the outer shell swatches. The studies did not use actual samples from the jackets to assess the decontamination efficiencies of the garments. The following study simultaneously evaluates the decontamination efficacies of different techniques on firefighters' jackets taken from the same sample set.

The effect of liquid CO<sub>2</sub> on compounds such as phthalates and PAHs was significant when compared with a conventional aqueous wash in Subsection 11.2. The modified surfactants from Subsection 10.2.2 demonstrated promising results on the bench-scale testing, especially for BaP and DEHP. The objective of the study was to evaluate the washing efficiency of the different washing techniques on the legacy gear. Till this point, all the studies were performed on liquid contamination. The particulate contamination from the structural fires may react differently to these methods.

## 12.2 *Materials and methods*

The following study was conducted in two parts. The first part of the study included an evaluation of the decontamination study on turnout suits from the Fire Department of New York (FDNY). The studies were conducted on outer shell material only. The sample sets included nine jackets which were divided into three categories based on the washing techniques they were subjected to.

The second part of the following study was the evaluation of the turnout suits from Broward County fire department. This study was also conducted on the outer shell of the suits. The sample sets included ten jackets and eight pants. This sample set was also divided into three categories according to the decontamination technique that they were subjected to.

The conventional wash and liquid CO<sub>2</sub> cleaning in both the studies were the same.

1. Conventional wash: CD-1 was used at 40±5°C for 60 mins. The UNIMAC 45 lb. washer-extractor (Model no-UWT045D4) was used for conventional wash. The total load for the wash cycle was 30 lbs. According to the recommended usage, 120 mL of CD-1 was used for the washing cycle. The washing cycle was 60 minutes which means the surfactant solution was in contact with the garments for 60 minutes. A separate rinse of 10 minutes

was added at the end of the washing. The conventional wash was according to the NFPA 1851 standard. After washing, all the samples were air-dried for 24 hours before doing the post-wash analysis.

2. Liquid CO<sub>2</sub> cleaning: The liquid CO<sub>2</sub> cleaning was done at Tersus Solutions (Denver, CO). The details of the method are described in Table 11-1.

The modified washes for FDNY and Broward County studies were different. The details of the methods are provided in the respective studies.

#### *12.2.1 FDNY turnout suits*

Retired turnout suits (outer shells only) from FDNY were used in the first study. Turnout suits were labeled as T1-T9. All nine turnout jackets were cut into halves. The first stage of the study was the extraction and analysis of the pre-wash samples from turnout jackets for qualitative and quantitative analysis. The extraction and analysis procedures were the same as described in section 8.2.3. Three swatches of 5 cm x 5 cm were cut from the left side of the suits. The schematic for the location from where swatches were taken for analysis is shown in Figure 12-1.

Different halves were washed with different types of washing techniques to study their efficacy. Every washing technique washed six halves. The three washing techniques used in the study were:

1. Conventional wash
2. Liquid CO<sub>2</sub> cleaning
3. Modified wash

The modified wash included using UNIMAC 45 lb. washer-extractor (Model no-UWT045D4). For this study, the commercial detergent CD1 was used at 65°C for 60 minutes.

The Mechanical agitation was included in the cycle where the G-force was less than 100. The modified method was similar to conventional wash in the washing cycles and G-force with a major change After washing all the samples were air-dried for 24 hours before doing post-wash analysis. For post-wash analysis, swatches of the same size adjacent to the previously cut samples were used (Figure 12-1). Table 12-1 shows the design of experiments indicating the combination of washing techniques and different halves of the gears.

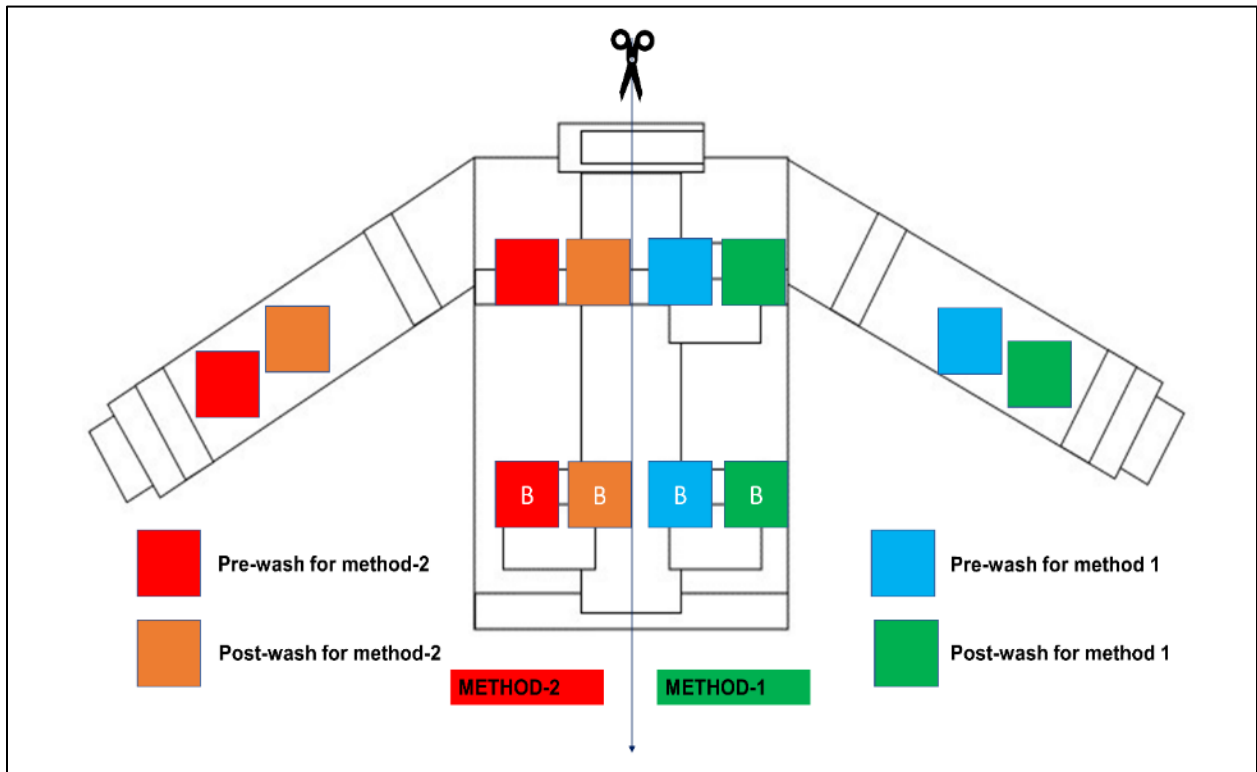


Figure 12-1: Schematic of samples from FDNY suits



Table 12-1: Summary of design of experiment

<b>Turnout suits (sample name)</b>	<b>Left part- method used</b>	<b>Right part- method used</b>
T1	Conventional wash	Liquid CO <sub>2</sub> cleaning
T2	Conventional wash	Liquid CO <sub>2</sub> cleaning
T3	Conventional wash	Liquid CO <sub>2</sub> cleaning
T4	Modified wash	Liquid CO <sub>2</sub> cleaning
T5	Modified wash	Liquid CO <sub>2</sub> cleaning
T6	Modified wash	Liquid CO <sub>2</sub> cleaning
T7	Conventional wash	Modified wash
T8	Conventional wash	Modified wash
T9	Conventional wash	Modified wash

12.2.2 Broward County turnout suits study

For the Broward County gear, ten jackets and eight pants were selected. From these samples, three swatches were removed for pre-wash analysis. The sampling strategy for this study was different than the previous one. For this study, the entire garment was washed with one single method, unlike the FDNY study where samples were cut in halves. The larger number of garments provided a larger sample set for the study. Thus, six whole garments were washed together using one washing technique. For post-wash analysis, the adjacent samples were taken. The left and right sides were chosen randomly for pre-wash samples. The schematic for sample locations is shown in Figure 12-2. The 18 specimens were divided into three groups and each group was washed with a different washing technique.

The three washing techniques used were:

1. Conventional wash
2. Liquid CO<sub>2</sub>
3. Modified wash

The modified method for this study included detergent D3 from 10.2.2 at  $65\pm 7^{\circ}\text{C}$  for 60 mins using UNIMAC 45 lb. washer-extractor (Model no-UWT045D4). A separate 10 mins of the rinsing cycle was added at the end of the washing cycle. The total load for the wash cycle was 30 lbs. The recommended amount was 24 oz for 32 gallons of water. The full-scale washer-extractor was using 44 gallons according to the database provided for the total washing cycle. Hence, the calculated amount was 976 mL. The volume of the detergent used was higher as compared to the CD1 used in the conventional wash.

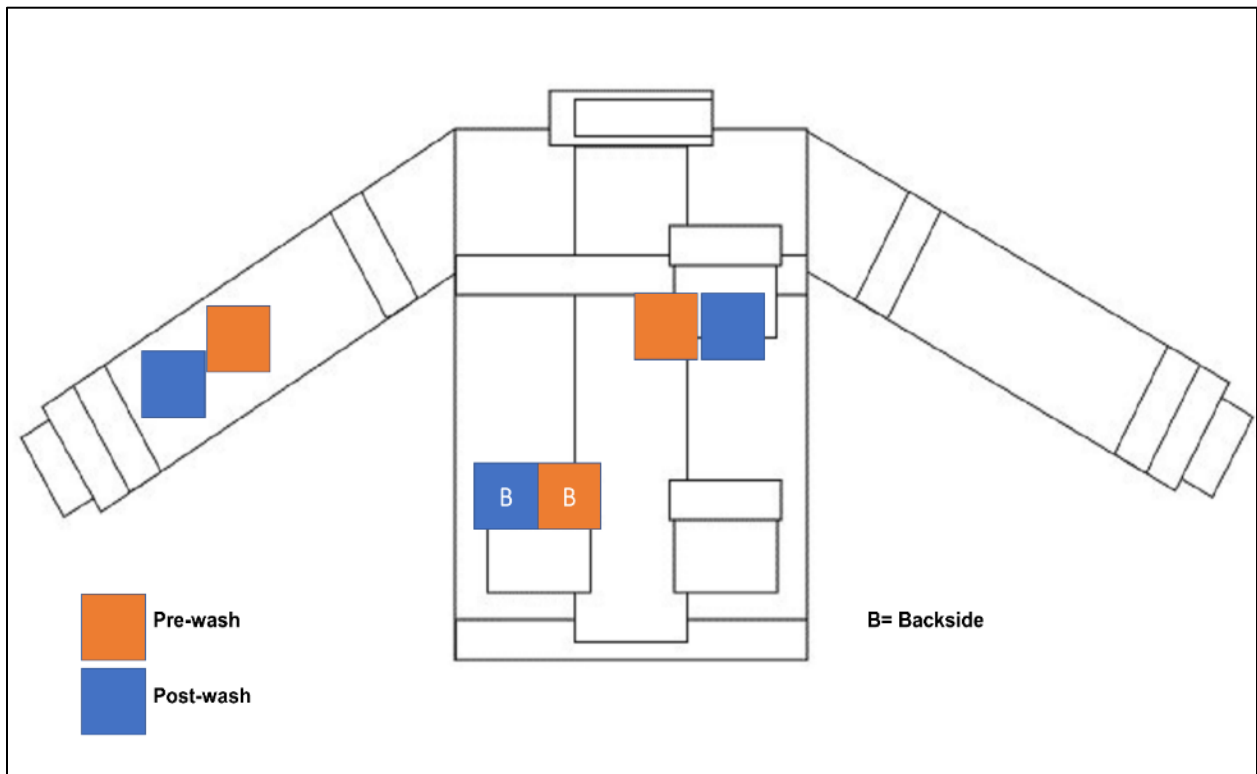


Figure 12-2: Schematic of samples from Broward County gears.

### 12.3 Results and Discussion

The data derived from the two studies FDNY turnout suits and Broward County suits are discussed below separately

### 12.3.1 FDNY turnout suits study

The turnout suit T3 was lost during transportation hence its pre-washed data was taken out of the study. In pre-washed samples, only DEHP was found. The concentration of DEHP on turnout samples is displayed in Figure 12-3. It was hypothesized that there would be a significant difference between washing methods. Although direct comparison between the pre-wash and post-wash samples would not be entirely sound due to high variation in the contamination, the washing efficiency results help in understanding the efficacy and shortcoming of a particular decontamination method. The spatial variation was high in all the samples as shown in Figure 12-3.

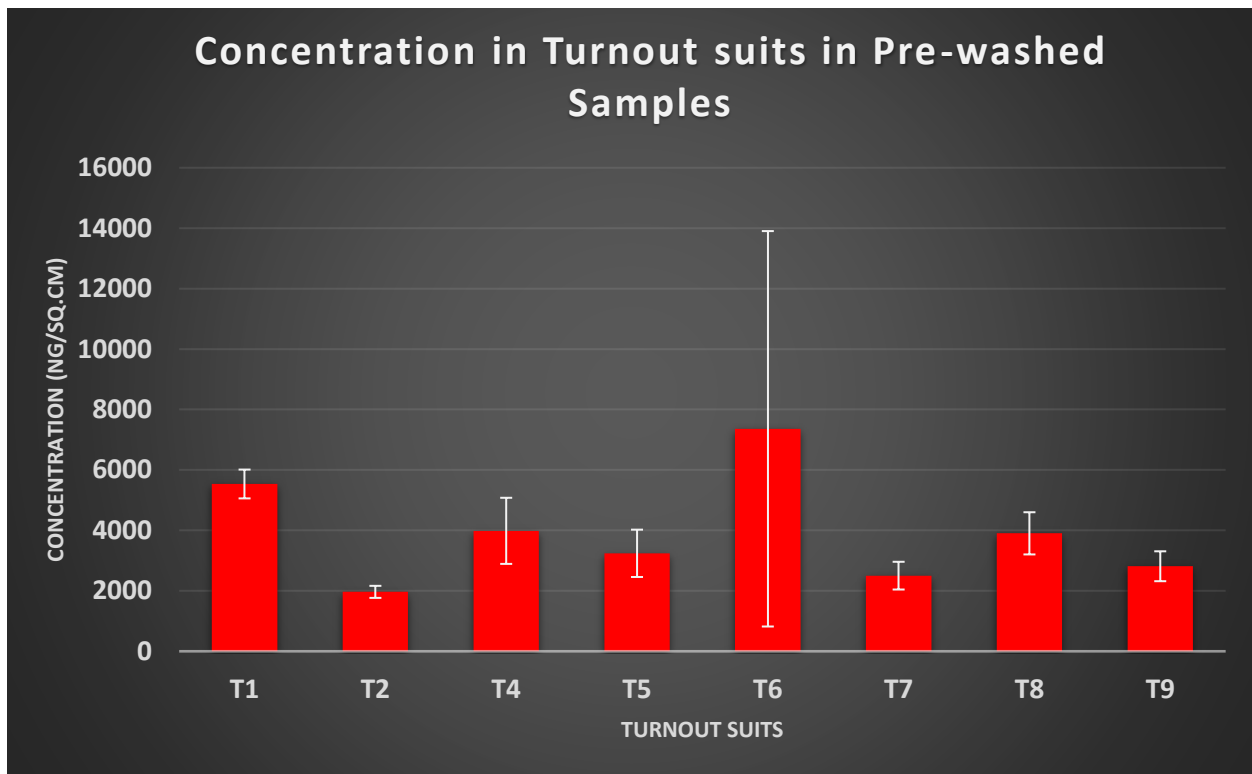


Figure 12-3: Concentration in Pre-washed samples.

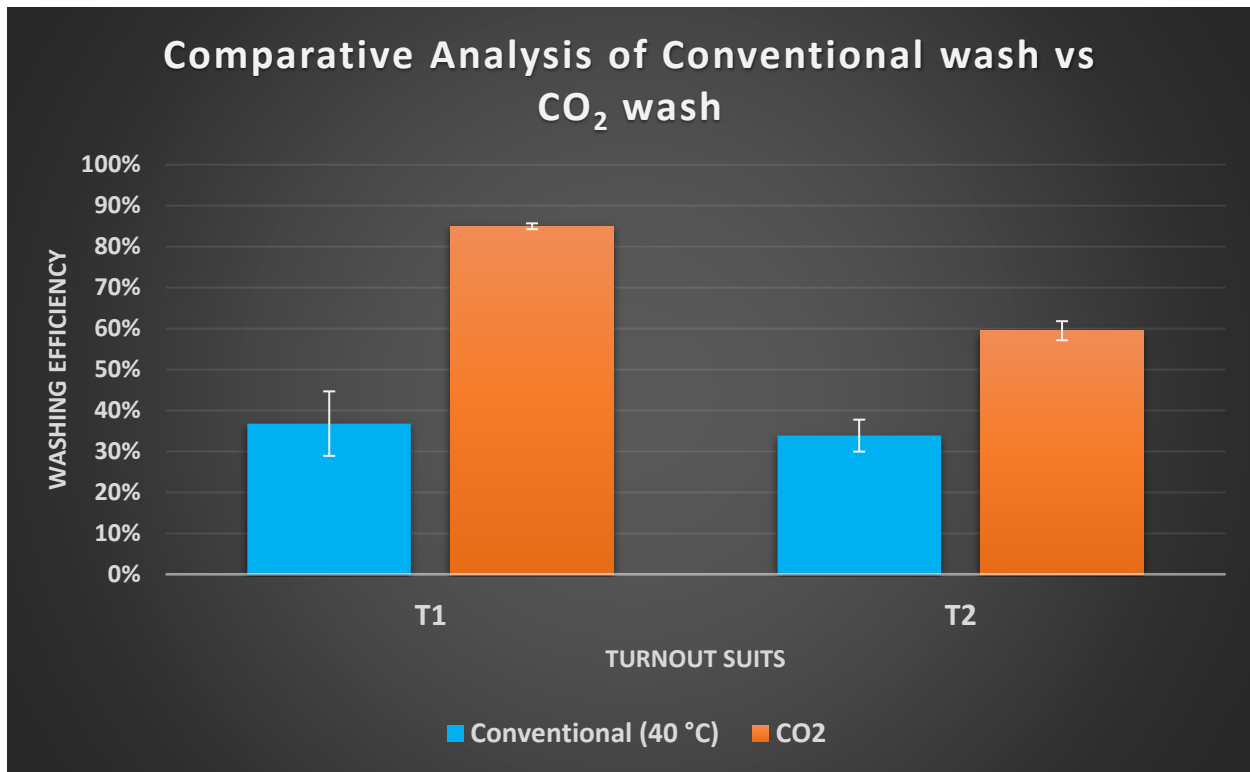
The two samples assuming unequal variances t-test at 95% confidence interval was used to check whether the results were statistically significant or not. The results are shown in Table 12-2.

The results indicated that for DEHP removal, liquid CO<sub>2</sub> washing was an effective technique when compared with aqueous washing. Increasing temperature for aqueous washing did not significantly improve DEHP removal.

*Table 12-2: t.test results for different washing methods.*

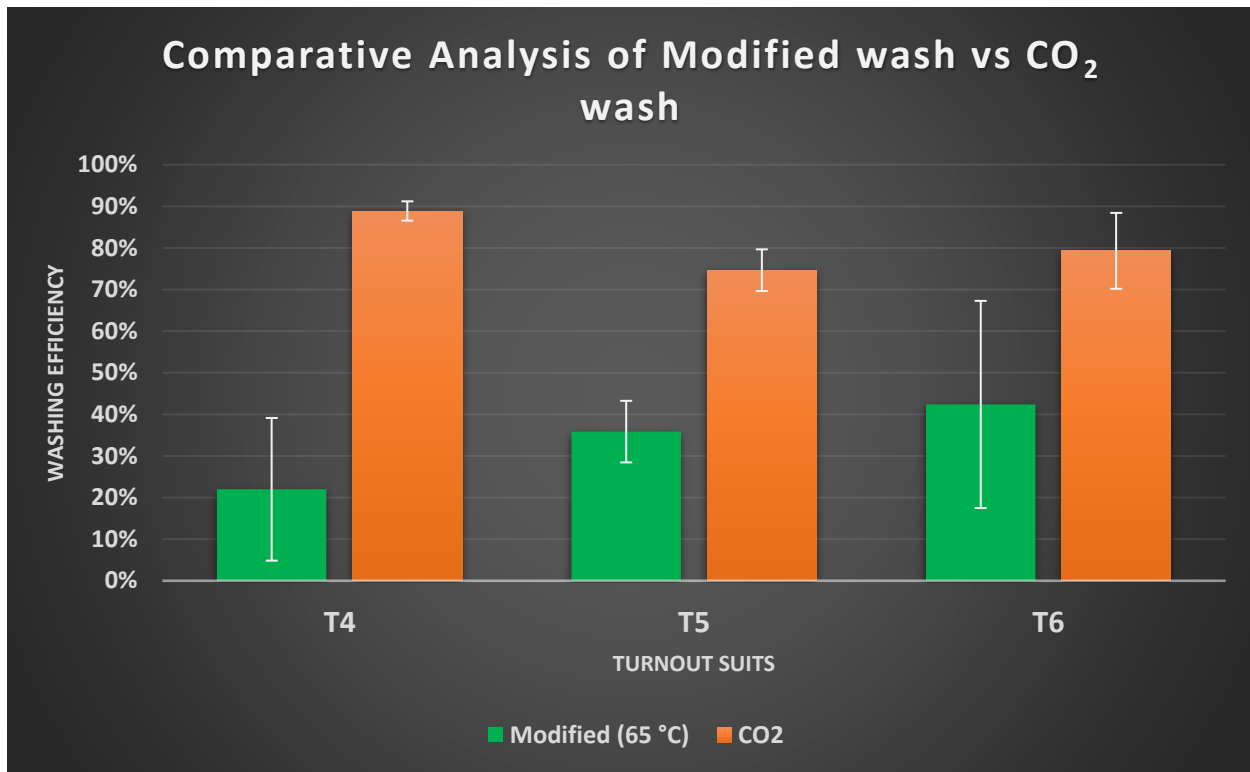
<b>Comparison</b>	<b>Results (<math>p &lt; 0.05</math>)</b>
Conventional wash vs Liquid CO <sub>2</sub>	Liquid CO <sub>2</sub> is statistically significant
Conventional wash vs Modified wash	Not significant
Modified wash vs Liquid CO <sub>2</sub>	Liquid CO <sub>2</sub> is statistically significant

The comparison of conventional wash and liquid CO<sub>2</sub>-washed samples is shown in Figure 12-4. The liquid CO<sub>2</sub>-washed samples demonstrated high washing efficiency for DEHP for turnout T1. For T2, the DEHP removal using liquid CO<sub>2</sub> was relatively low due to low contamination in pre-wash samples (Figure 12-3). This may be due to variations in the concentration in pre & post-wash samples. The high pressure and non-polar nature of liquid CO<sub>2</sub> helped in removing DEHP from the fabric.



*Figure 12-4: Comparative Analysis of Conventional wash vs CO<sub>2</sub> wash.*

For comparison of modified washed samples with liquid CO<sub>2</sub> washed samples, the results are illustrated in Figure 12-5. The error bars for modified washed samples from T4 and T6 denoted values 17.15% and 24.95% respectively that highlighted the variation in contamination. For liquid CO<sub>2</sub>-washed samples, the error bars were small in size that indicated low variation in these samples. There are possibly two reasons for high variations: (1) The samples themselves were contaminated unevenly, (2) During washing, the cross-contamination occurred from other samples.



*Figure 12-5: Comparative Analysis of Modified wash vs CO<sub>2</sub> wash.*

A direct comparison of washing at different temperatures (40°C vs 65°C) was illustrated in Figure 12-6. It indicated that for T7, there was a significant difference for a modified wash. For T8 and T9 samples, the results were comparable. It indicated a similar trend as seen in Figure 9-20.

The increase in temperature did not have a significant impact on removing DEHP. Thus, using CD-1 there is a limited potential in removing DEHP in particulate form using conventional washing. The average of different washing methods is shown in Figure 12-7. It showed an increasing trend when the type of washing method is changed from conventional to modified to liquid CO<sub>2</sub>.

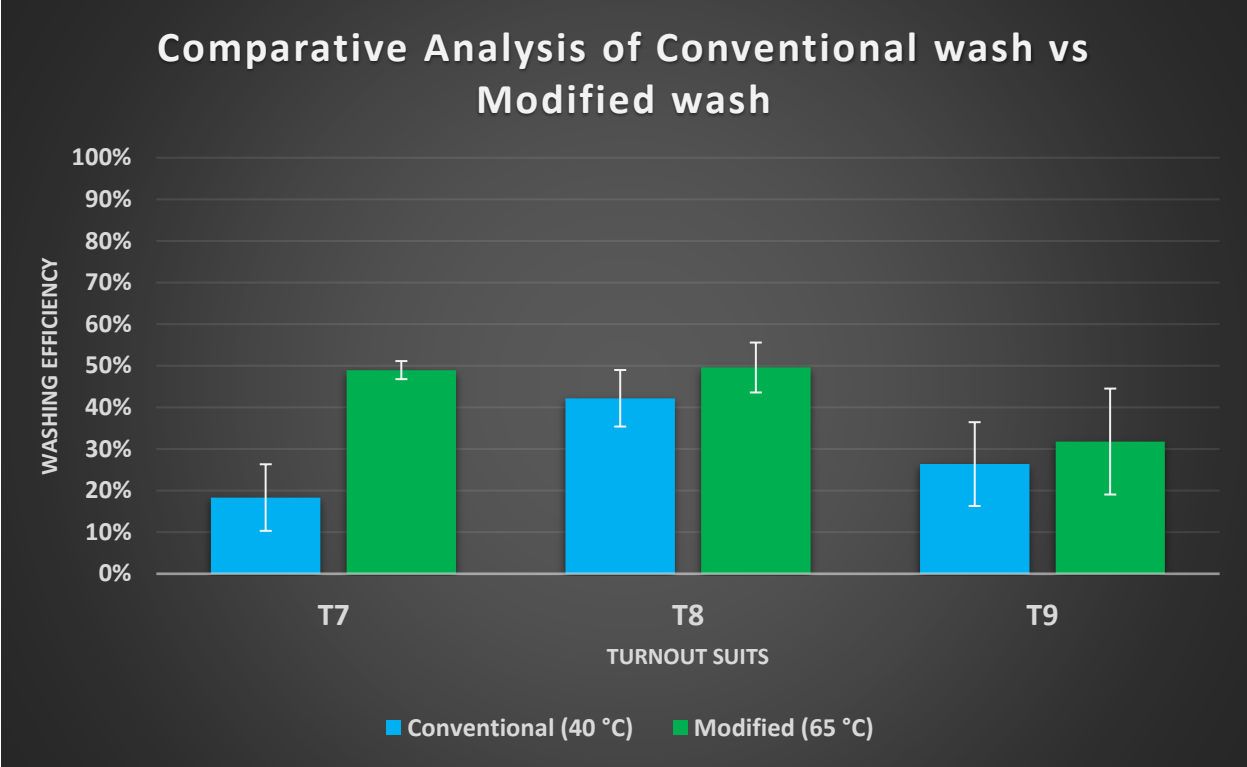


Figure 12-6: Comparative Analysis of Conventional wash vs Modified wash.

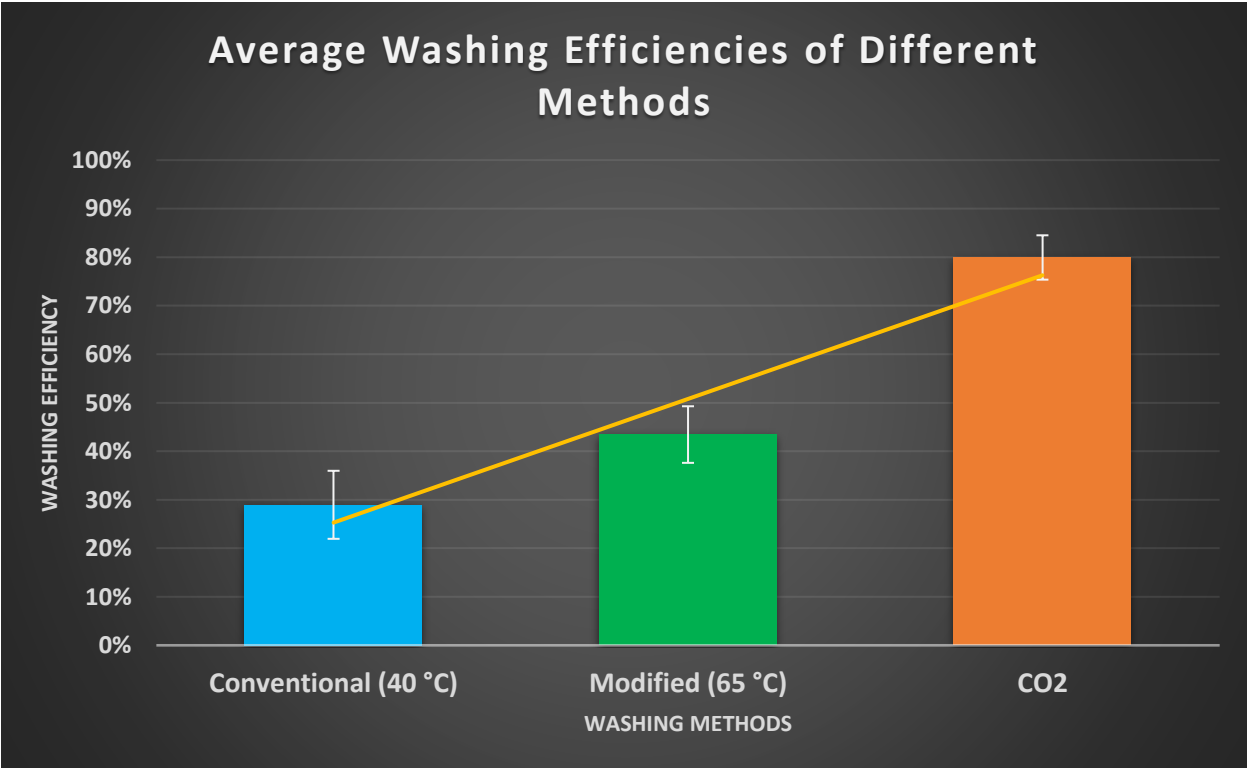


Figure 12-7: Average Washing Efficiencies for different methods.

### 12.3.2 Broward County gears study

The pre-wash samples analysis showed the presence of phthalates: DBP, BBP and DEHP. The concentration of the samples varied considerably as seen in Figure 12-8. DEHP was present in higher amounts as compared to DBP and BBP. The detection limits for the phthalates are given in Table 12-3.

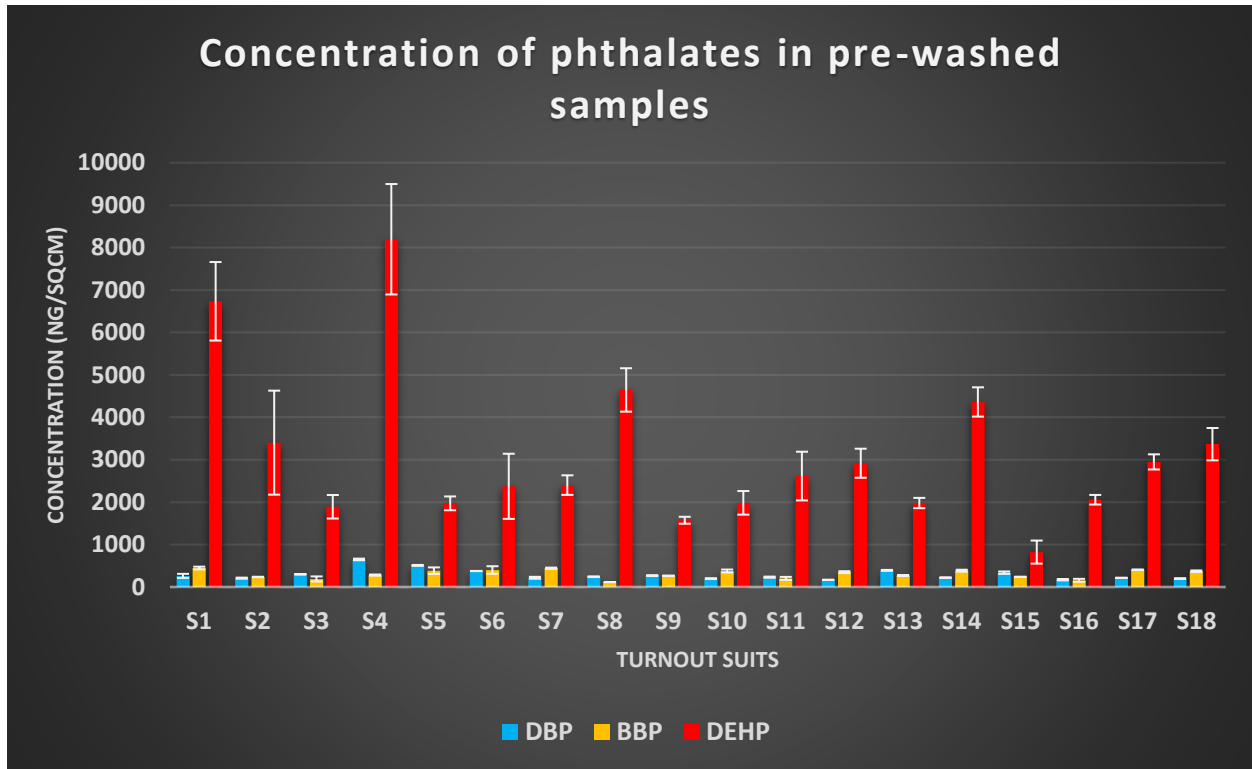


Figure 12-8: Concentration of phthalates on Broward County turnout suits.

Table 12-3: Detection limits for phthalates.

	LOD		LOQ	
	(ng/μL)	ng/cm <sup>2</sup>	(ng/μL)	ng/cm <sup>2</sup>
<b>DBP</b>	0.19	76	0.66	264
<b>BBP</b>	0.17	68	0.58	232
<b>DEHP</b>	0.1	40	0.33	132



### 12.3.2.1 Conventional wash

The average washing efficiency for the phthalates using conventional wash is shown in Figure 12-9. Only for S4, S5 and S6, the values are above 0% indicating that the concentration of phthalates, majorly DBP, in post-washed samples for S4, S5, S6 was less than that in pre-washed samples. Thus, only DBP was removed from the samples using conventional aqueous washing.

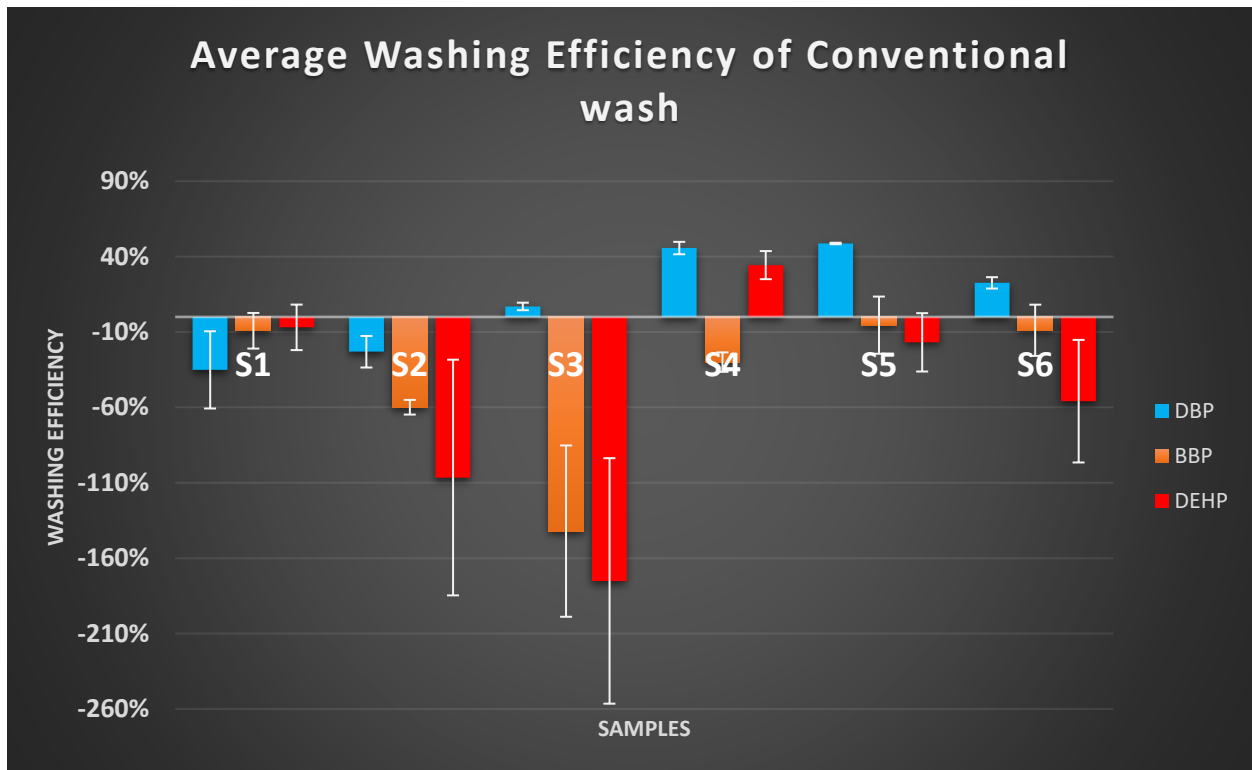


Figure 12-9: Average Washing Efficiency of Conventional wash.

The individual concentrations for DBP are shown in Figure 12-10. For samples S1, S2 the DBP concentration was high in post-wash samples. This might be due to the cross-contamination in the garments or the samples had a higher concentration in the first place. For samples S5 and S6, the difference between pre-wash and post-wash samples was high.

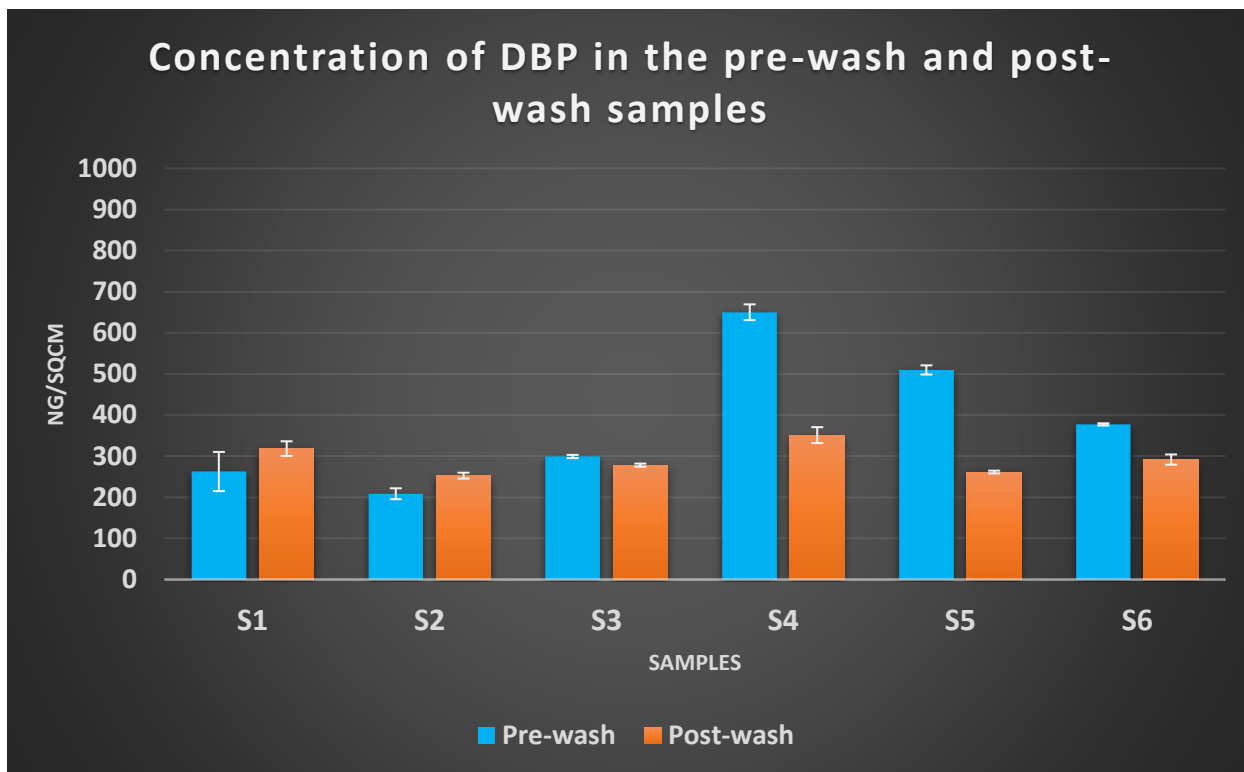


Figure 12-10: Comparative Analysis of Concentration of DBP for conventionally washed samples.

The concentration of BBP in the garments is shown in Figure 12-11. The concentration of BBP in S5 and S6 in pre-washed samples was high and for post-wash, it did not decrease. The post-wash concentration in samples S1 to S3 increased drastically indicating that there was significant cross-contamination for DBP.

The garments were heavily contaminated with DEHP (Figure 12-12). The average concentration in S4 was around 8196 ng/cm<sup>2</sup>. The error bars indicated the value of 1301ng/cm<sup>2</sup> for DEHP contamination in S4. Thus, the spatial variability was high in these garments. For post-wash samples, there was a significant decrease in S4 but the other samples indicated an increase in the concentration for post-wash samples. This proved that the contaminants may get redeposited on the garment. Thus, the overall concentration for DEHP did not decrease which

was seen in the lab-scale studies. This was consistent with the analysis that the conventional wash had limited potential in removing phthalates.

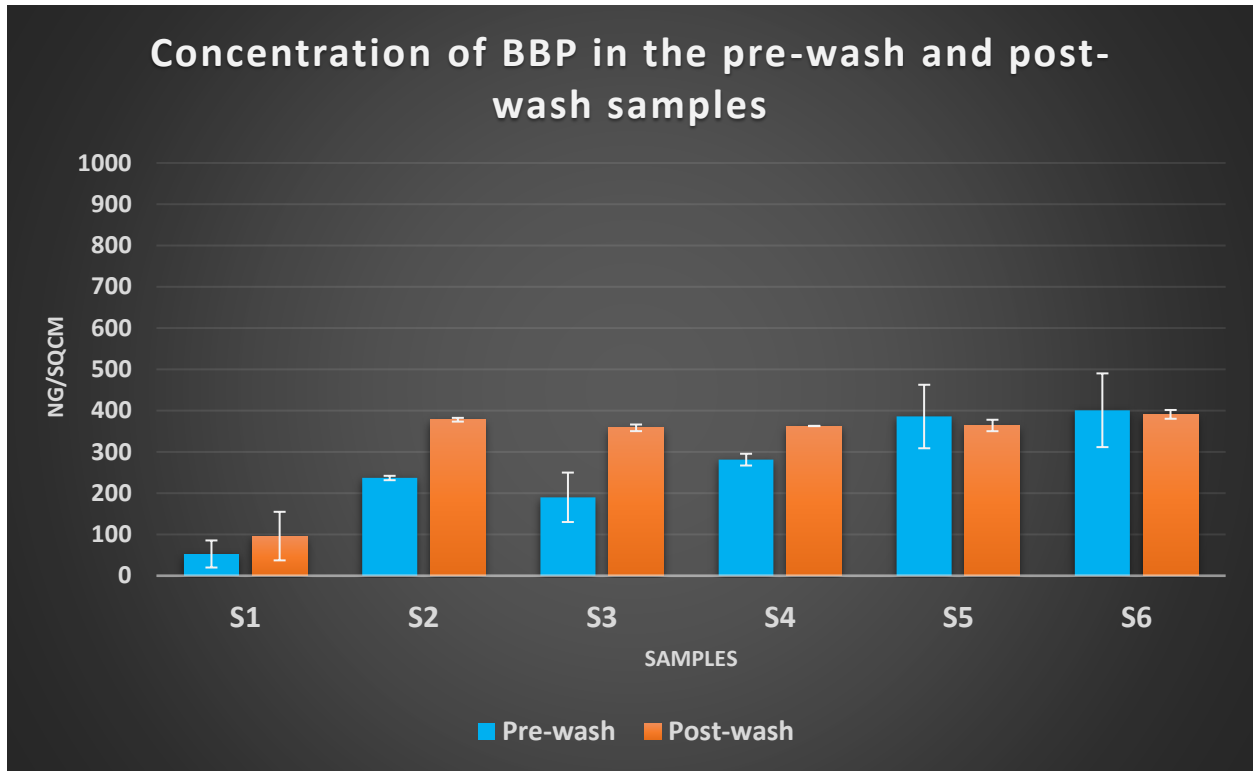


Figure 12-11: Comparative Analysis of Concentration of BBP for conventionally washed samples.

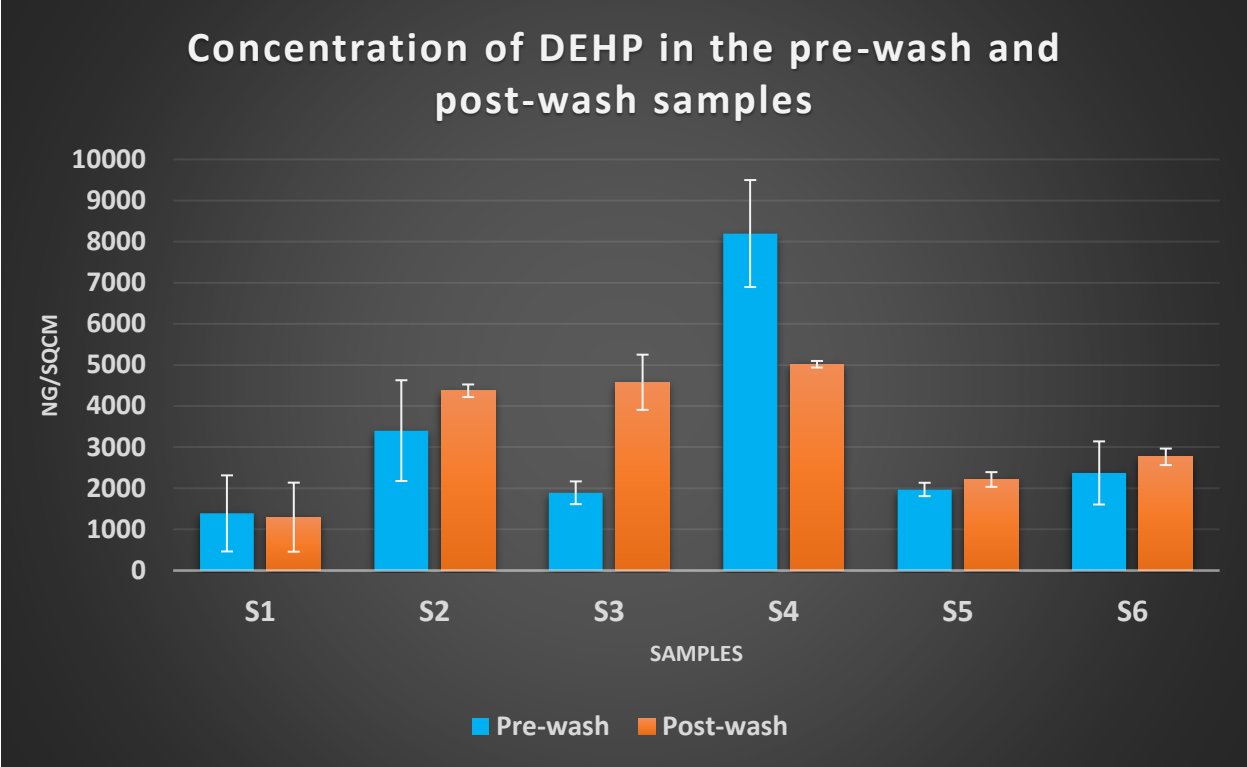


Figure 12-12: Comparative Analysis of Concentration of DEHP for conventionally washed samples.

When the values of average efficiencies for all the garments were taken for individualized phthalates (Figure 12-13) it showed a decreasing trend from DBP>BBP>DEHP that highlighted the importance of hydrophobicity of the phthalates as seen previously in bench-scale and full-scale studies. The important difference between the pilot-scale studies and the legacy gear studies was the particulate contamination in legacy gear. Phthalates have high  $K_{OW}$  values and that emphasizes their affinity towards organic material such as dirt and particulates from the smoke as compared to water. Thus, the effect of mechanical action can improve the removal of particulates. The major trade-off for high mechanical action can be the bulk migration of dirt particles from one location to another that can dislodge the contaminants and affect the calculations.

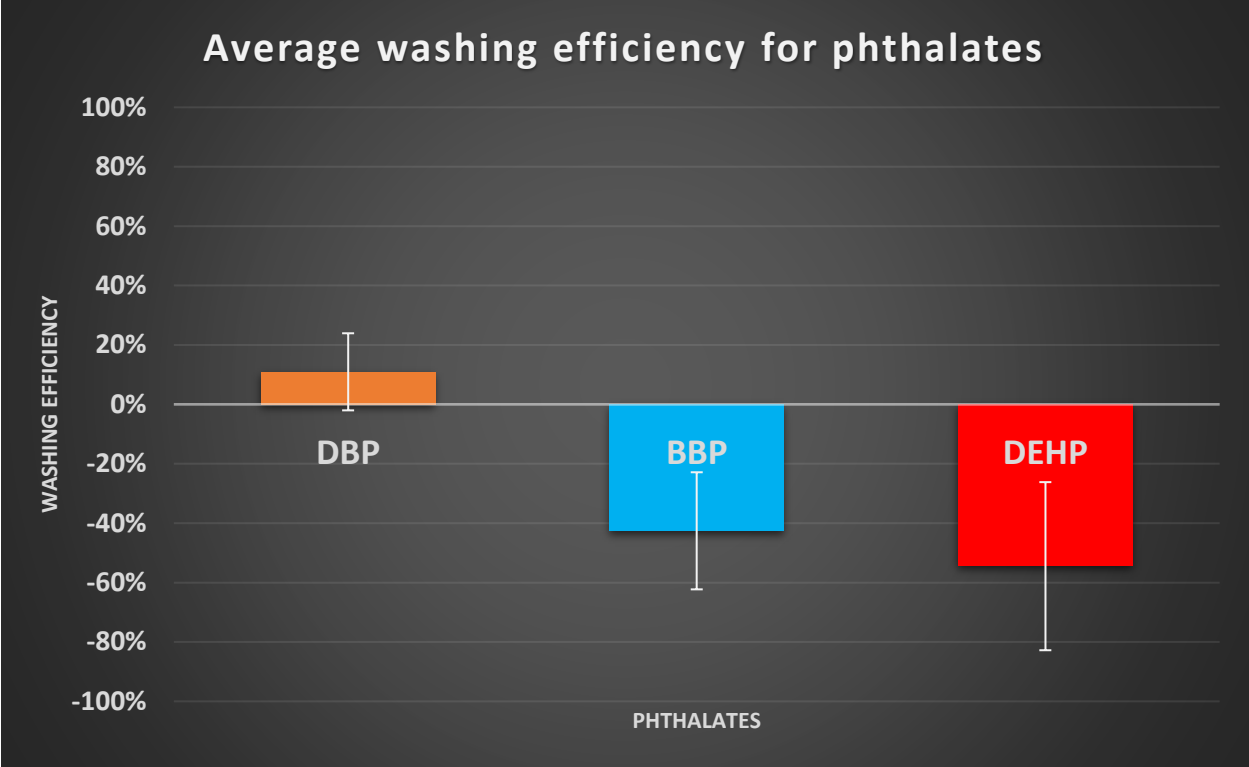


Figure 12-13: Average washing efficiencies for phthalates using conventional washing.

The visual comparison of the conventionally washed samples is shown in Figure 12-14. The dusty feel on the fabric was reduced after cleaning the garments using conventional wash. From the visual comparison, there was no significant damage to the garment using the conventional washing method. Some of the reflective trim on the garment was damaged but it might be since the garments were considerably old.



Figure 12-14: Effect of conventional wash on turnout suits (a)pre-wash (b)post-wash.

#### 12.3.2.2 Modified wash

The average washing efficiencies for phthalates for individual samples are shown in Figure 12-15. The D1 surfactant removed BBP and DEHP in significant amounts as compared to the conventional washing. The washing efficiency for DBP decreased which was different from the bench-scale testing results for this surfactant. Considering the results for the bench-scale testing (Figure 10-5) it can be concluded that the DBP was present in very high amounts on the fabric itself that the samples used for post-wash analysis contained DBP in greater quantities than the pre-wash samples as shown in Figure 12-16.

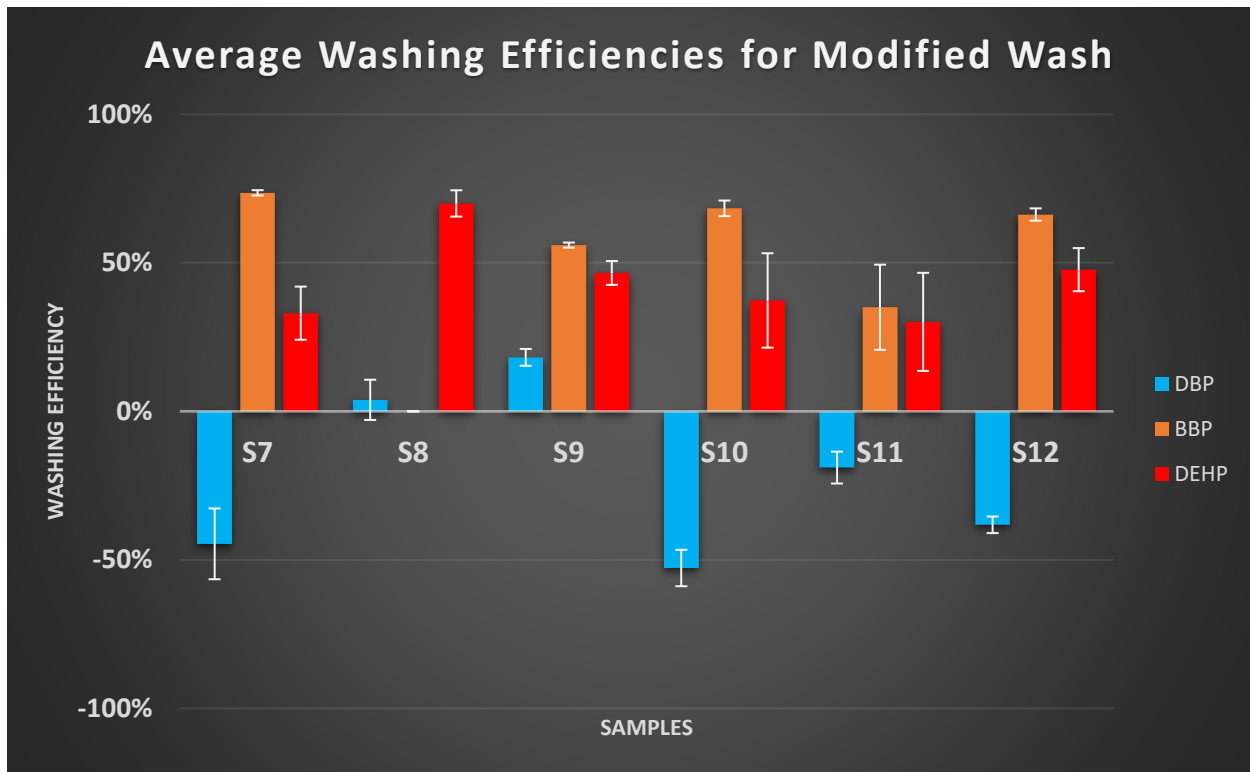


Figure 12-15: Average washing efficiency for phthalates using modified wash.

For BBP, the concentration for post-wash samples was calculated using LOQ/2 values thus, the modified washing was efficient in removing BBP from the fabrics (Figure 12-17). Similarly, DEHP was removed from the fabrics in moderate amounts as illustrated in Figure 12-18. These findings were consistent with the bench-scale testing.

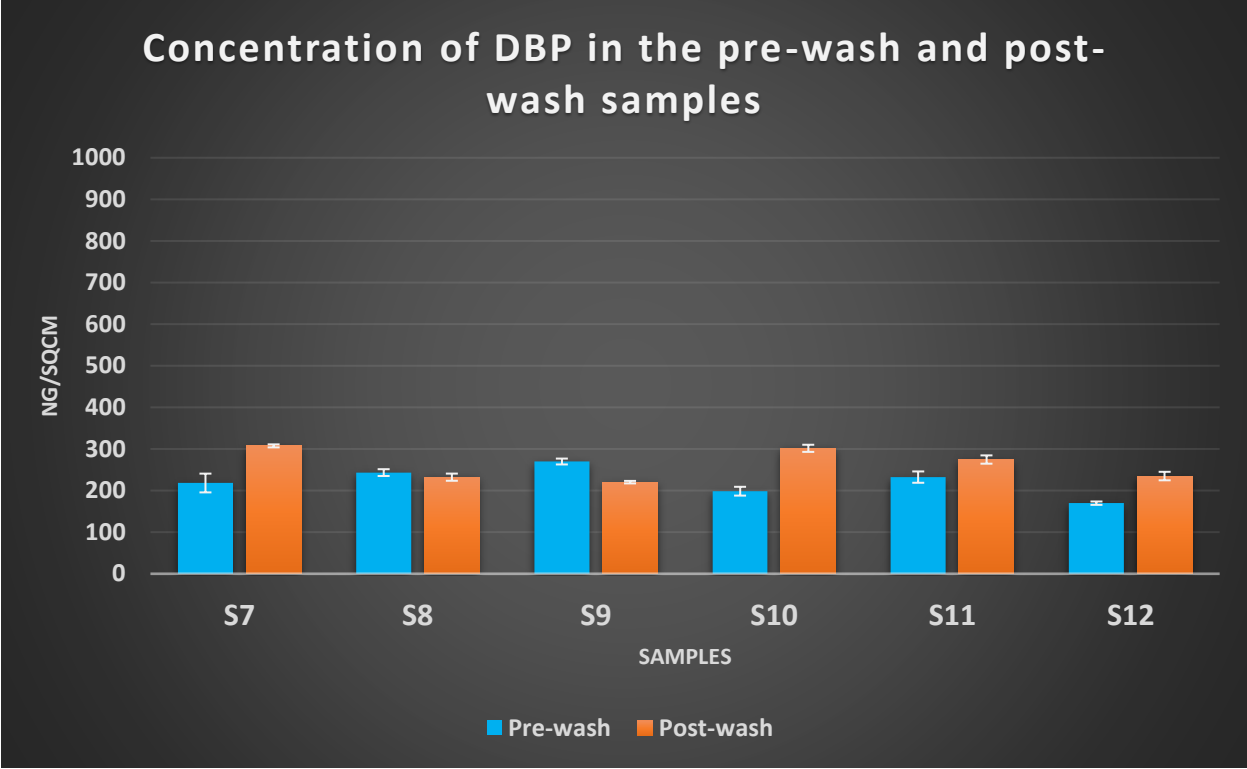


Figure 12-16: Comparative Analysis of Concentration of DBP for modified washed samples.

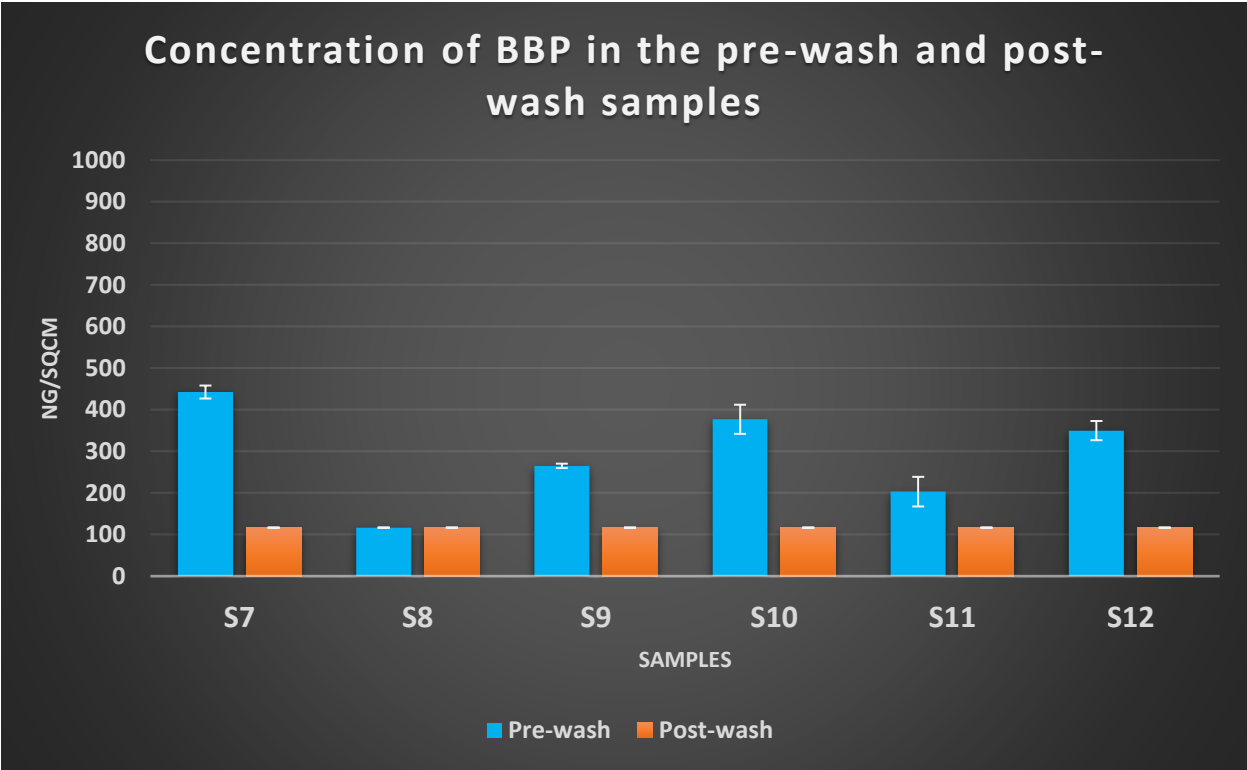


Figure 12-17: Comparative Analysis of Concentration of BBP for modified washed samples.



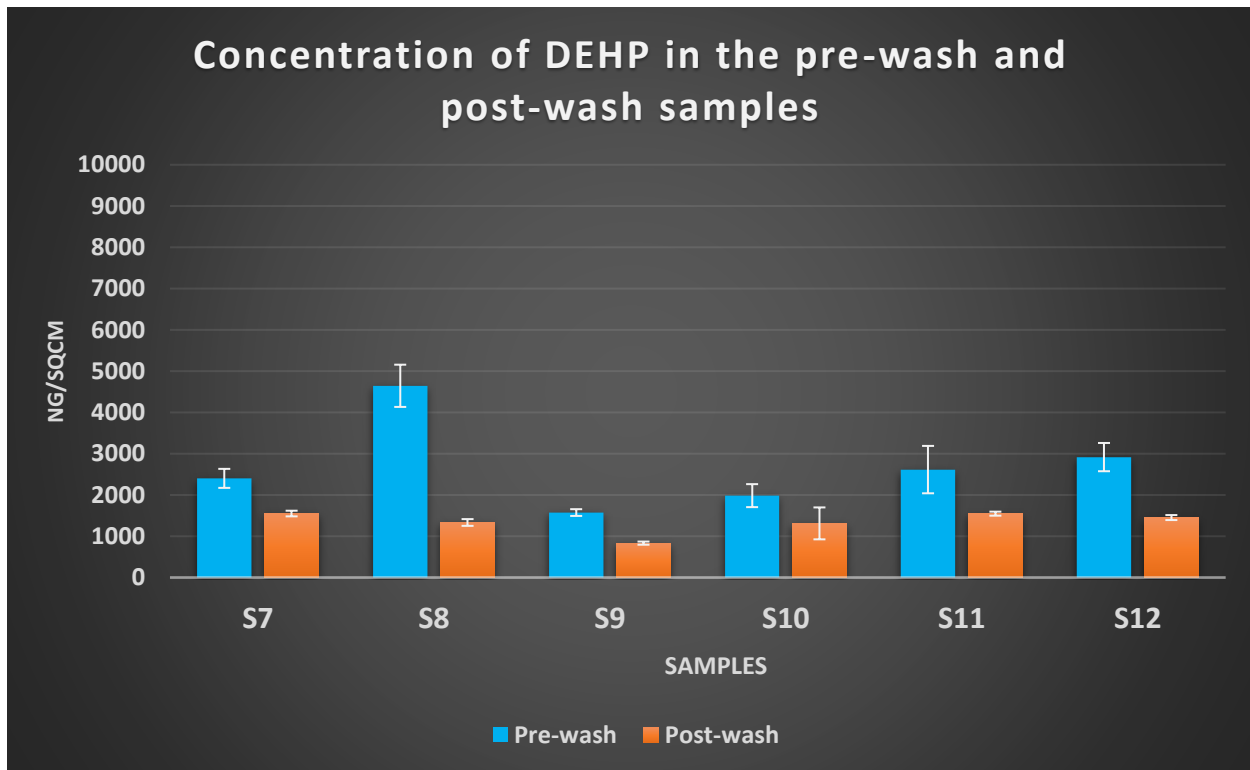
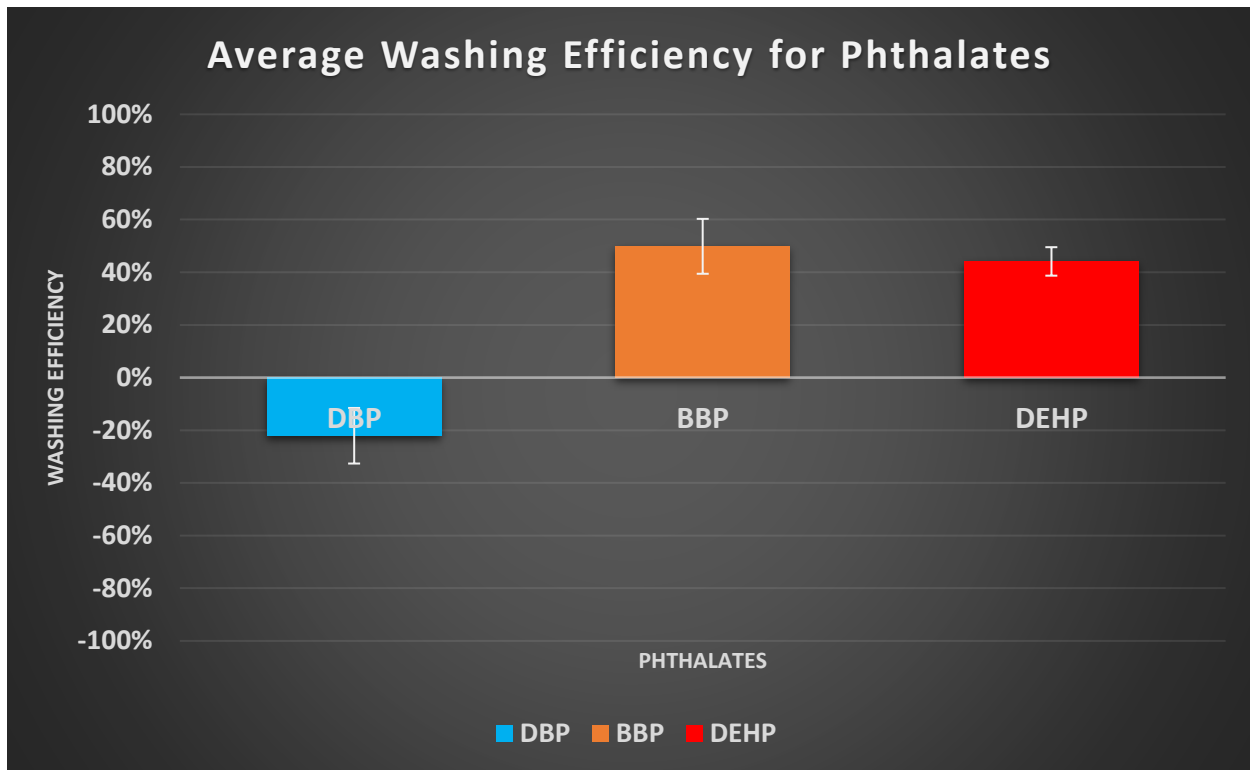


Figure 12-18: Comparative Analysis of Concentration of DEHP for modified washed samples.

The washing efficiency for phthalates in descending order was BBP>DEHP>DBP (Figure 12-19). The primary reason for such high removal might be the damage caused by using such a high concentration of surfactant D3. The outershell fabric felt thinner and the reflective trim on the outershell materials was completely stripped off as seen in Figure 12-20. This may have contributed to the removal of particles hence high washing efficiency was achieved.



*Figure 12-19: Average washing efficiencies for phthalates using modified washing.*

The major drawback of using such a high volume of surfactant was its negative impact on the turnout suit as illustrated in Figure 12-20. The color of the outer-shell material faded. The reflective trims on the outer shell were destroyed. Thus, using a high volume of the surfactant at such a higher temperature (65°C) for longer washing durations can degrade the turnout suits. Although the particulate contamination disappeared the trade-off for using modified washing at higher concentration was significantly higher on the negative side. This study highlighted the adverse effect of higher concentration of the surfactant on the the outer shell material.



Figure 12-20: Effect of modified wash on turnout suits (a)pre-wash (b)post-wash.

#### 12.3.2.3 Liquid CO<sub>2</sub>

The liquid CO<sub>2</sub> cleaning demonstrated high washing efficiency for phthalates as illustrated in Figure 12-21. The washing efficiency trend increased from DBP to DEHP. The values for BBP for post-wash analysis used were LOQ/2. For sample S16, there were negative values for average washing efficiency since the concentration for DBP and DEHP in the pre-washed samples was below detection limits hence LOQ/2 value was taken. DBP was beyond the detection limit in two of three samples and DEHP in one sample. To avoid skewing of the data one sample containing these compounds beyond the detection limit was taken out. So, from sample S16 only two swatches were used in the analysis. Overall liquid CO<sub>2</sub> washing worked better in removing the phthalates as compared to the other two methods used. The reverse order of higher washing efficiency in phthalates when compared with the controlled study from section 11.2 indicated that the liquid CO<sub>2</sub> being non-polar in nature showed greater affinity for DEHP and BBP since they were more hydrophobic. Also, the literature on dry cleaning applications

has stated that the redeposition of particles in liquid CO<sub>2</sub> contributed to the low particulate removal [139], [163].

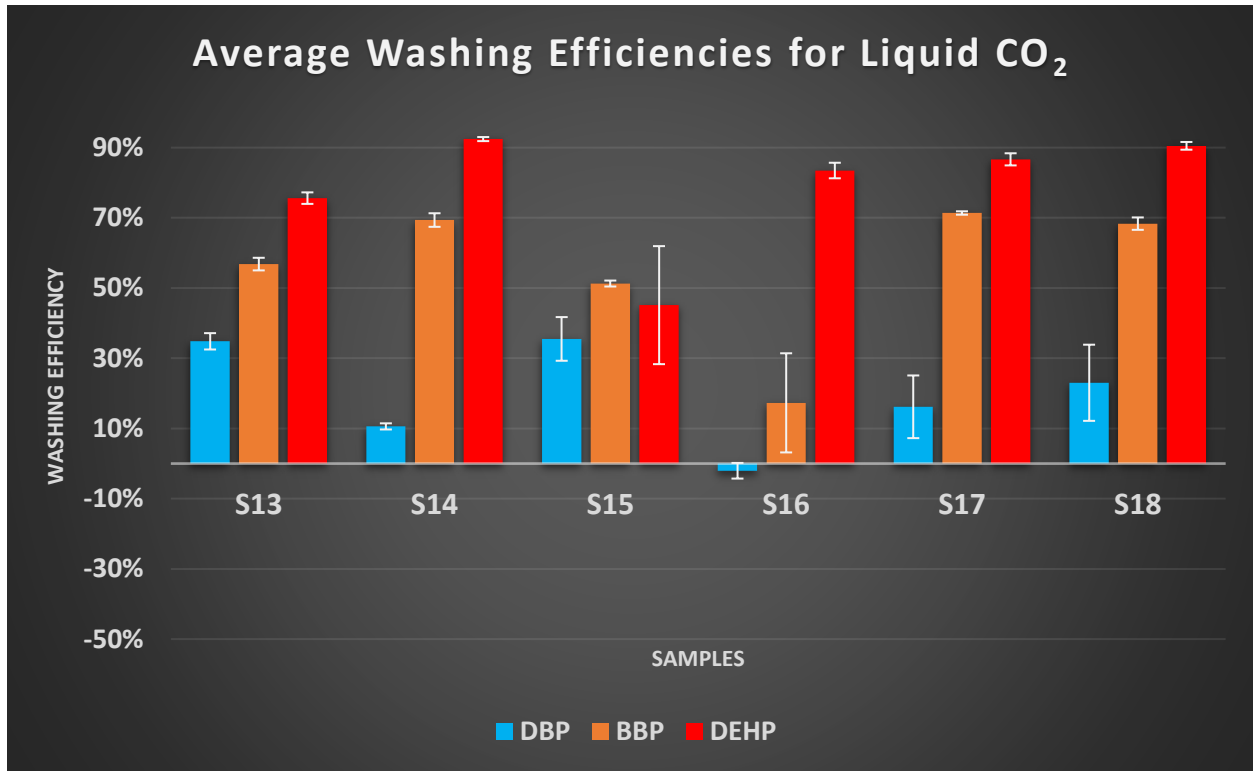


Figure 12-21: Average washing efficiency for phthalates using liquid CO<sub>2</sub> wash.

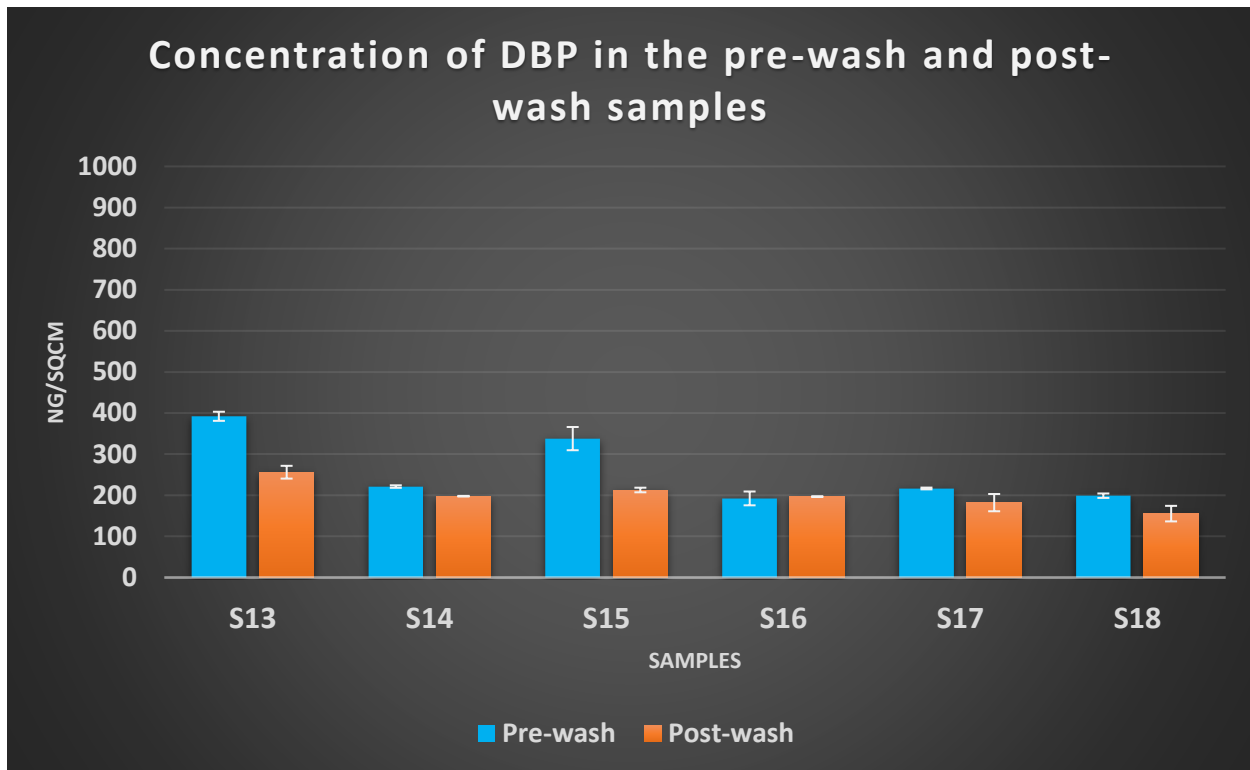


Figure 12-22: Comparative Analysis of Concentration of DBP for Liquid CO<sub>2</sub> washed samples.

The concentrations of DBP for pre-wash and post-wash are shown in Figure 12-22. The level of contamination present for DBP in pre-wash and post-wash samples was comparable hence demonstrating low washing efficiency. This showed a deviation from the controlled study. The low concentration of DBP may be approaching an equilibrium state. Also, for the particulate contamination, DBP may have a limited affinity for liquid CO<sub>2</sub> due to the absence of any polarity in the mix. In Figure 12-22, only samples S13 and S15 showed a significant reduction. For all other samples, the values did not decrease much and are present in the comparable amount around 200 ng/cm<sup>2</sup>.

In contrast to DBP, the concentration of BBP in post-washed samples was beyond the detection limits (Figure 12-23). This was consistent in all the samples. This showed that BBP was removed effectively from the samples.

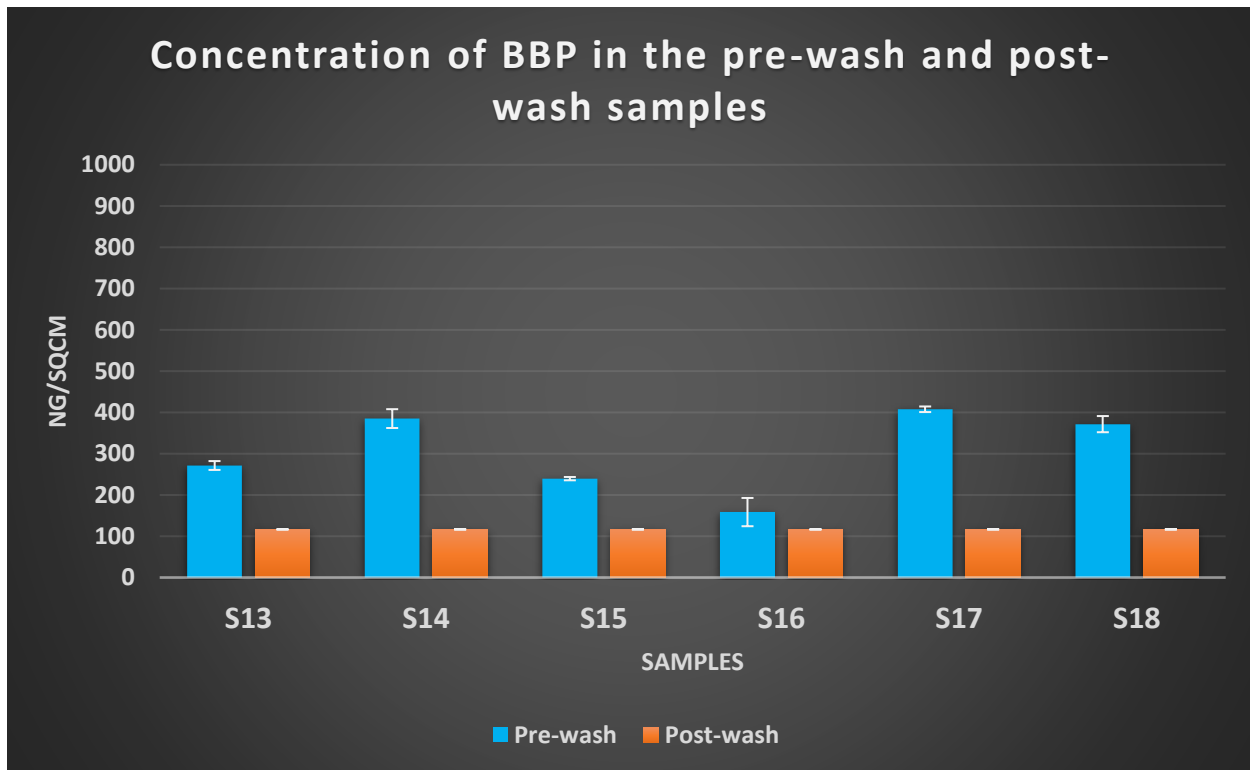


Figure 12-23: Comparative Analysis of Concentration of BBP for Liquid CO<sub>2</sub> washed samples.

Thus, the average washing efficiency for individualized phthalates for all the samples is shown in Figure 12-25. The BBP and DEHP showed better removal than DBP. The standard error for DEHP was very high as compared to the other two phthalates that indicated huge variation in DEHP contamination. If sample S16 is removed from the data, the average washing efficiency for DEHP increased from 44% to 78% and the results were statistically significant for a 95% confidence interval when t.test was used. The order of contamination in decreasing order is DEHP >BBP>DBP. The rate of desorption from the fabric was directly proportional to the concentration present thus the DEHP is getting desorbed quickly followed by BBP and then DBP.

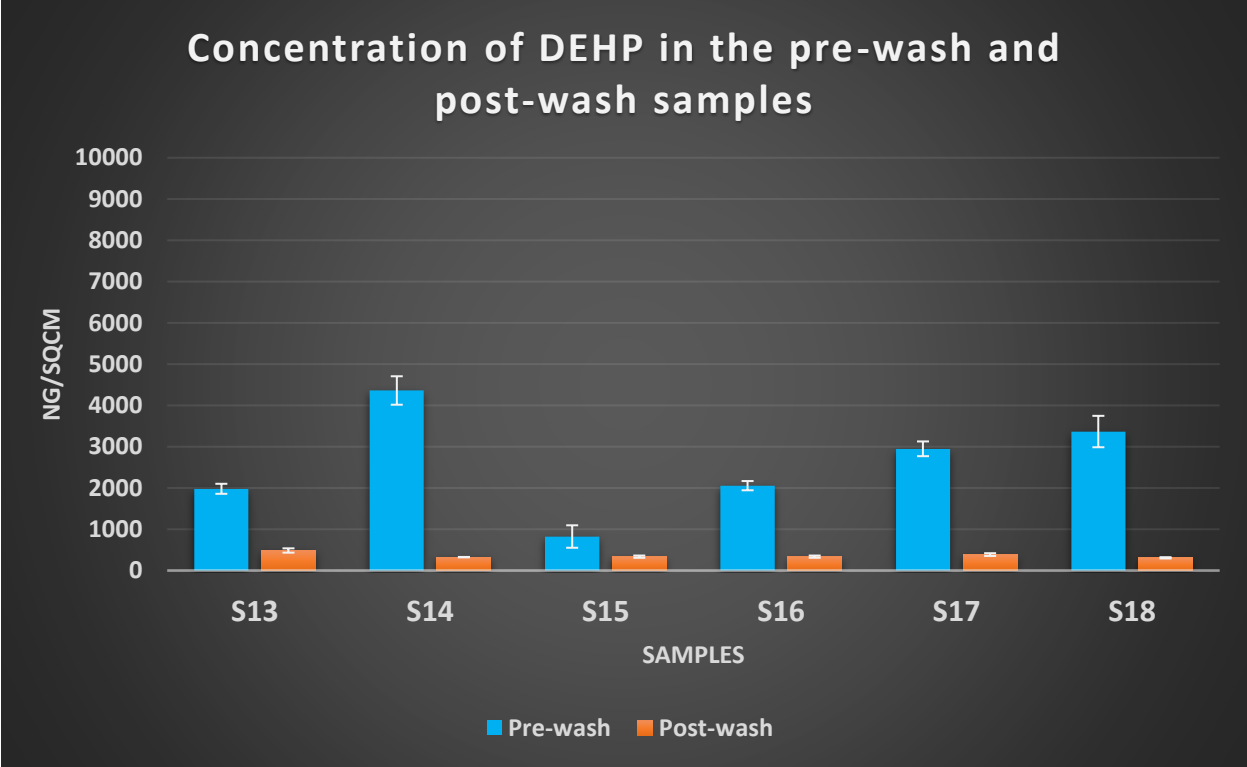


Figure 12-24: Comparative Analysis of Concentration of DEHP for Liquid CO<sub>2</sub> washed samples.

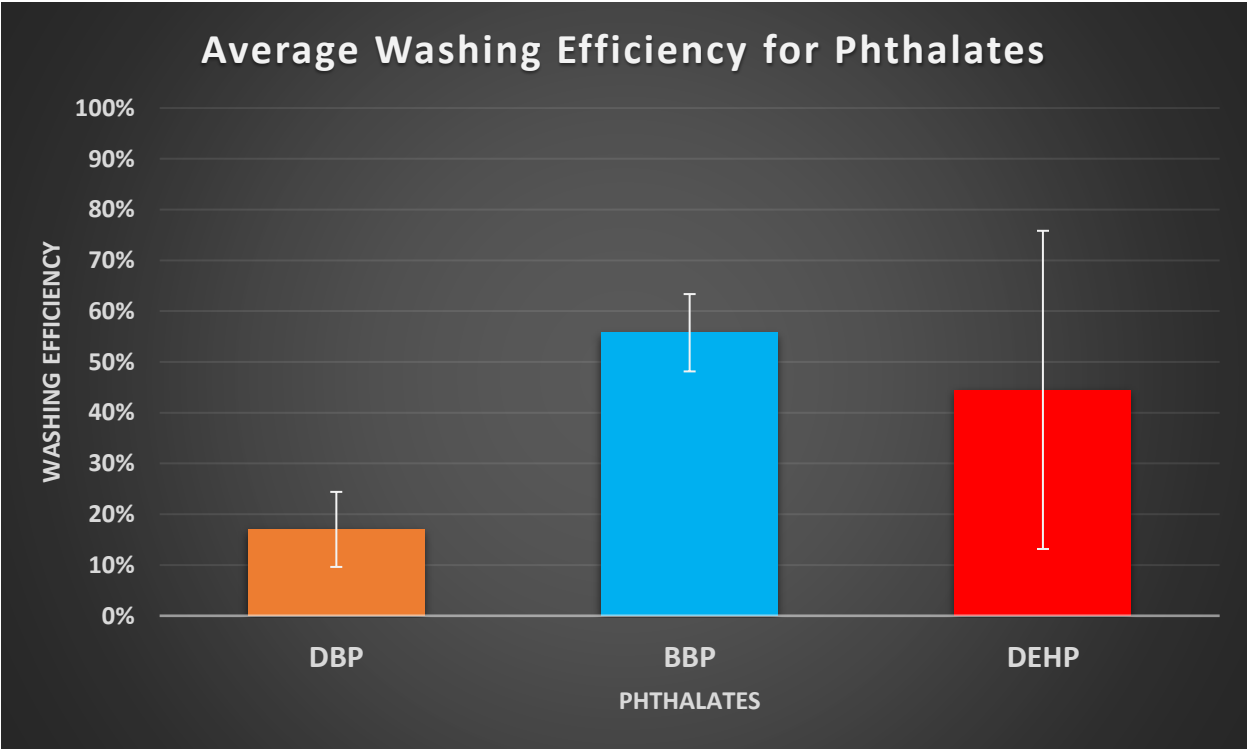


Figure 12-25: Average washing efficiencies for phthalates using liquid CO<sub>2</sub> washing.

The visual comparison of the pre-wash and post-wash samples is shown in Figure 12-26. There was no significant impact of the liquid CO<sub>2</sub> wash on the turnout suit. The dark color of the particulate contamination spots on the jacket faded and became lighter. Using visual comparison, it is difficult to spot a difference between washed and unwashed garments.



*Figure 12-26: Effect of liquid CO<sub>2</sub> wash on turnout suits (a) pre-wash (b) post-wash.*

#### 12.4 **Conclusion**

The study showed the effects of different washing methods on real-world samples. The compound DEHP was present in both studies. The studies showed the importance of choosing surfactants. The increasing temperature for FDNY did not have a significant impact on cleaning DEHP from the garment while for Broward County gears increasing temperature with modified surfactant dramatically improved the removal of contaminants. Thus, the concentration and chemistry of the surfactant need to be investigated further.



The level of contamination varied considerably between garments and even in the same garment. The spatial variability of the contaminants was a major hindrance in evaluating the washing efficiency of any method on real-world samples. The average of contamination from multiple swatches helped in understanding the contamination and evaluation of the washing methods. The aqueous washing method using conventional surfactants did not improve the removal of DEHP significantly. This result was consistent with the bench-scale and full-scale studies. Liquid CO<sub>2</sub> did work effectively in removing phthalates. For FDNY studies, the results were statistically significant and liquid CO<sub>2</sub> worked better than conventional washing.

For the Broward County gear study, all three target phthalates were present. The nature of contamination (liquid versus particulate) is an important aspect that needs to be investigated. The particulate contamination may have been a cause of deviation in the results when the results of this study were compared with a controlled study. For liquid CO<sub>2</sub>-washed samples, DBP was not removed effectively when compared with BBP and DEHP. The low contamination of DBP may have slowed the transfer of the contaminants from the fabric to the liquid. The modified wash did improve the removal of phthalates which was due to the high concentration of the surfactant although the damage to the garment was severe when washed with such high concentration.

The results of washing efficiency of liquid CO<sub>2</sub> were higher as compared to the other methods used in these studies. When the results are compared with the controlled study from section 11.2.1, the washing efficiency of liquid CO<sub>2</sub> for particulate contamination is lower. The washing efficiency for particulate contamination for liquid CO<sub>2</sub> is lower due to (1) redeposition [163], (2) the absence of forces to overcome the interaction between particles and substrate [139]. Redeposition can be defined as a transfer of soil particles from one textile to another and is one of the limitations of liquid CO<sub>2</sub> [163]. The Van der Waal interactions can be present

between soil particles and fabric is strong in liquid CO<sub>2</sub> since it has a low dielectric constant. This contributes to poor particle removal in liquid CO<sub>2</sub> cleaning [139].

The pre-wash analysis in both studies showed the presence of phthalates. Considering the results from the controlled study and assuming that the retired turnout suits were washed regularly before, the phenols may have been removed from the garments previously. PAHs such as BaP and pyrene are partitioned towards the particulate matter. If these garments were subjected to on-scene decontamination, PAHs may have been removed from the garment during that process. Thus, the efficacy of the on-scene decontamination technique needs to be investigated further.

## **Chapter 13: Assessment of Different Washing Procedures on the Durability of the Turnout Suits**

*Excerpts from the following chapter were part of the AATCC conference 2020*

### **13.1 Introduction**

The firefighting profession is one of the challenging professions that include working in a hazardous environment. The protective clothing is the firefighter's armor that reduces the risk of injury in a dangerous environment. The coats and pants are referred to as turnout gear. The turnout gear consists of three elements: outer shell, moisture barrier and a thermal liner that are specified in the NFPA 1971 standard on Protective Ensembles for Structural Firefighting and Proximity Firefighting [20]. The outer shell protects firefighters from abrasion, cuts and flame protection. The materials used are polybenzimidazole (PBI), Nomex®, Kevlar®. The finishes are applied on the outershell that is water and oil repellent. The moisture barrier offers protection from water, chemicals and is made of polytetrafluoroethylene, polyurethane attached to the substrate. The thermal liner is the innermost layer that provides thermal protection from ambient heat [20].

The supplementary accessories include reflective trims, product labels. The trim is an important element of the turnout gear as it aids the wearer's ability to be noticed by fellow firefighters during fire suppression activities. The product label provides instructions to help firefighters in taking care of the turnout gears. Thus, the elements enhance the functionality of the turnout gear. The NFPA 1851 Standard on Selection Care and Maintenance (SCAM) requires the retirement of the ensemble and its elements no more than 10 years from the date of the manufacturer [188]. Thus, the durability of the turnout gear and its elements is very important. The NFPA 1851 standard (SCAM) recommended washing guidelines from the durability

perspective. The standard has added a requirement of the turnout suit receiving at least two advanced cleaning per year [188].

The washing procedures did not remove the contaminants that the turnout suits are exposed to during structural fire hazards [12]. Hence, the current research tested different parameters to improve the cleaning procedures. The comparative analysis of different washing methods on real-world samples demonstrated that using specialized cleaning methods such as liquid CO<sub>2</sub> wash improved the decontamination of the turnout suits. Simultaneously tuning the parameters such as increasing the temperature and using a modified surfactant performed well also. The history of the real-world samples was not available hence the assessment of the durability was incomplete.

The following study aimed to assess the impact of multiple washing of any technique on the durability of the turnout suits. The outer shell material is accessorized with reflective trims, product labels to ensure the complete safety of the firefighters as well as provide them instructions to maintain their turnout suits. The turnout suits need to last more than 5 years since they are very expensive. Thus, before incorporating any changes in the cleaning procedure its impact on durability needs to be investigated.

## 13.2 *Methods*

### 13.2.1 *Sample Preparation*

To study the impact of various washing methods on the durability of the turnout suits and their accessories, outer shell swatches of size 26-inch x 26-inch were used. The outershell material used was PBI MAX™ Gold with a durable water repellent finish. These swatches were used to simulate the turnout suits in a controlled manner. The yellow-silver reflective trims were imported and stitched to the outershell material. The garment is shown in Figure 13-1. The

product labels were heat pressed on the opposite side of the trim (considered as an inner side) at 400°F for 10 seconds as shown in Figure 13-2. Every set contained five swatches all accessorized with trims and four of those were accessorized with product labels due to the limited availability of the product labels.



*Figure 13-1: Outershell swatch with reflective trim.*

The swatches in every set were subjected to 30 washes for the respective method. Ballast material was used to make up the volume to 30 lbs. It was decided that if there was any significant damage for 30 washes then another set of fabrics would be subjected to 15 washes using the same method to compare the results. The ballast material included outershell material jackets. The objective was to assess the impact of the washing on the garment and the

assumption was the turnout suits receive washing once every month. A separate set of four swatches was prepared which was kept unwashed and was used as a controlled sample set for future measurements.

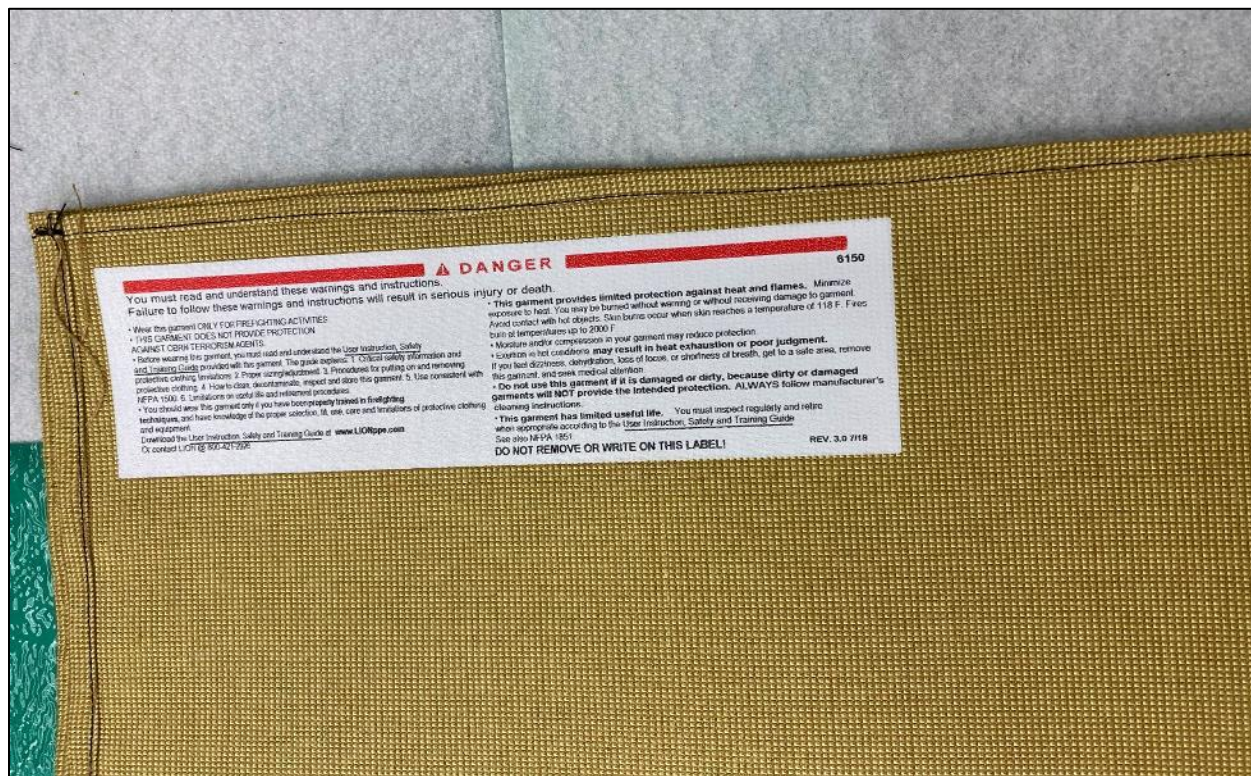


Figure 13-2: Product label heat sealed.

The washing methods were as follows:

(1) Conventional

40°C for 60 minutes in the UNIMAC washer-extractor was used. The detergent chosen was CD-1. The volume of the detergent was 120 mL. The washing cycle included 60 minutes followed by 10 minutes. This meant that the surfactant solution was in contact with the garment for 60 mins. For regular conventional wash, the surfactant solution contact time varies from 20 minutes to 40 minutes, and then rinsing with fresh water is followed. The period of contact was kept 60 mins just to be consistent with the bench-scale and the full-scale level methods used in Section 9.4.2

## (2) Modified

65°C for 60 minutes in the UNIMAC washer-extractor was used. The detergent chosen was CD-1. The D1 detergent was not available at that time hence, CD-1 was used which was incorporated in the FDNY study. The volume of the detergent was 120 mL. The washing cycle included 60 mins followed by 10 mins. Similar to the conventional wash, the garment and surfactant solution was in contact for 60 mins.

## (3) Liquid CO<sub>2</sub>

For liquid CO<sub>2</sub>, two sets were shipped to Tersus Solutions. The details of the method are provided in Table 11-1. One set was subjected to 15 washes and one was subjected to 30 washes. Post-washing all the fabric swatches were sent back for analysis.

### *13.2.2 Physical testing of the samples*

#### *13.2.3 Tearing strength*

For tearing strength, the ASTM D5587 method was used. The test method covered the measurement of the tearing strength of the fabric by the trapezoid procedure. From every set, 10 swatches (5 in warp direction and 5 in weft direction) of size, 3-inch x 6-inch were cut randomly.

#### *13.2.4 Breaking strength*

For breaking strength, the ASTM D5034 method was used. The test method determined the breaking force for the fabric. From every set 10 swatches (5 in warp direction and 5 in weft direction) of size, 4-inch x 6-inch were cut randomly.

#### *13.2.5 Goniometer*

To study the impact of different washing procedures when subjected multiple times to the water repellent finish, contact angle measurements were used. The Analytical Services

Laboratory at Wilson College of Textiles was contracted for this testing. The Goniometer FDS Corporation Data physics OCA system was used. For every set, 18 replicates of the fabrics were used of 1 cm diameter.

#### *13.2.6 Spectrophotometer $L^*$ , $a^*$ , $b^*$ values*

The color measurement of the samples was performed on a spectrophotometer: Spectro-Guide sphere gloss S (Model 68-15-10). The  $L^*$  value represents the lightness and is measured from 0 (black) to 100 (white). The  $a^*$  and  $b^*$  value represents the redness-greenness and yellowness-blueness of the fabric. For every set, the values were measured for the outer shell material, the reflective trim (yellow and silver strip), and the whiteness of the product label. Every measurement was an average of measurements taken from random places on the sample.

### **13.3 Results and Discussion**

#### *13.3.1 Tearing strength*

The testing results are illustrated in Figure 13-3. The tearing force was measured in Newtons. There was a significant drop in the tearing strength of the samples washed with conventional and modified methods. The results were statistically significant ( $p < 0.05$ ) in both directions. Similarly, modified wash results were statistically significant ( $p < 0.05$ ) in both directions. The results indicated that the surfactant solution when kept for a longer period in contact with fabric can damage it. Generally, the conventional aqueous wash would not have 60 mins of contact time with the fabric. These results indicated the worst-case scenario for a conventional wash. For liquid  $\text{CO}_2$ , there was no significant damage in the tearing strength. The liquid  $\text{CO}_2$  set washed 15 times did show a loss in the tearing strength as compared to the 30 washes set which was an inconsistency and was attributed to a research artifact.



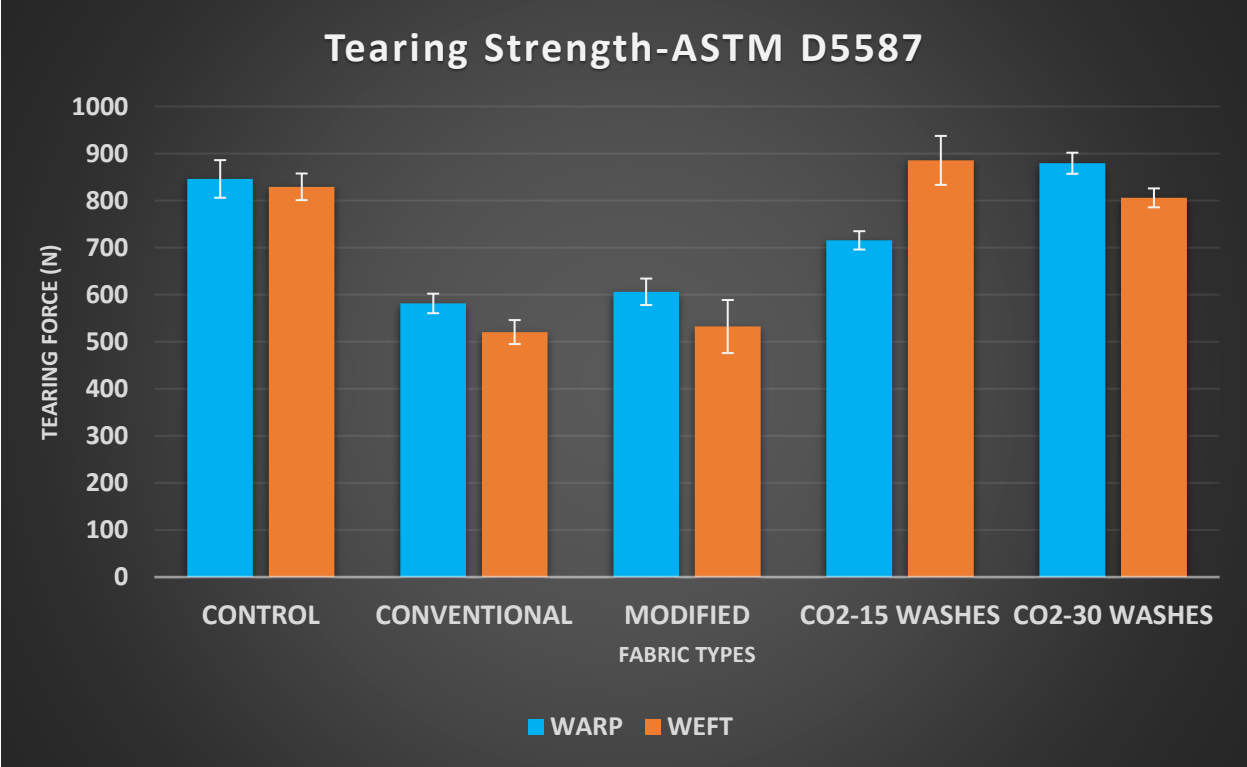


Figure 13-3: Tearing strength testing results.

13.3.2 Breaking strength

The peak load for the breaking strength testing was calculated in Newtons and the results are illustrated in Figure 13-4. Except for modified washed samples, all the other sample sets showed comparable results with unwashed samples. Thus, the breaking strength was not affected for both conventional and liquid CO<sub>2</sub> cleaning. When the modified wash was considered, the only difference in the parameter was the higher temperature (65°C). Thus, the higher temperature has an adverse effect on the breaking strength of the outershell material. The results were statistically significant (p<0.05) when compared with control samples.

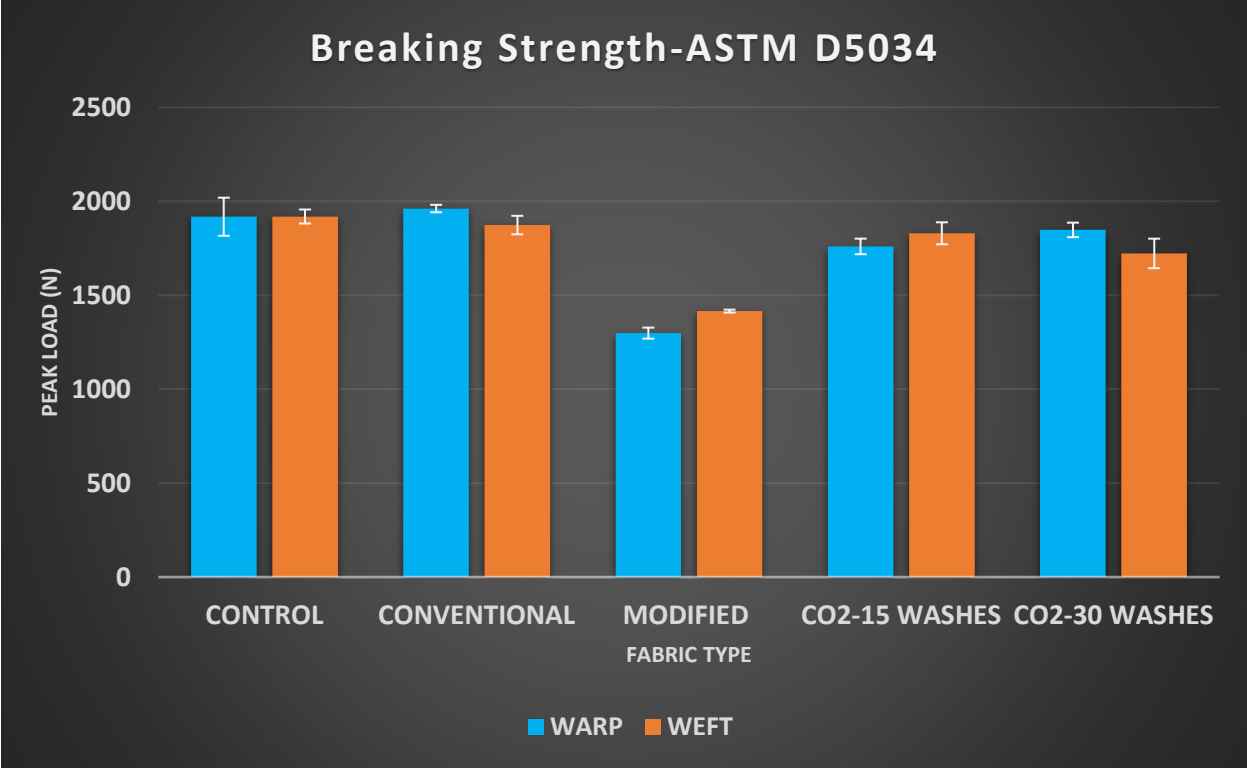


Figure 13-4: Breaking strength testing results.

13.3.3 Goniometer

The Goniometer results are illustrated in Figure 13-5. The control samples demonstrated water repellency as shown in Figure 13-6. The fabrics washed multiple times using conventional and modified wash demonstrated hydrophilicity as shown in Figure 13-7 and Figure 13-8, respectively. It meant that the surfactant solutions when used for a longer washing duration removed the water repellent finish. Remember for the conventional wash, there was a longer than usual contact period time with the fabric. This demonstrated the extreme case for a conventional wash. It also meant that over the years the conventional wash can affect the water repellent finish. The liquid CO<sub>2</sub>-washed fabrics demonstrated comparable results with the control samples. Thus, the liquid CO<sub>2</sub> wash used in this process did not have any impact on the water replant finish applied on the outershell material. The contact angle measurement for liquid CO<sub>2</sub>-15 washes & 30 washes is shown in Figure 13-9 & Figure 13-10 respectively.

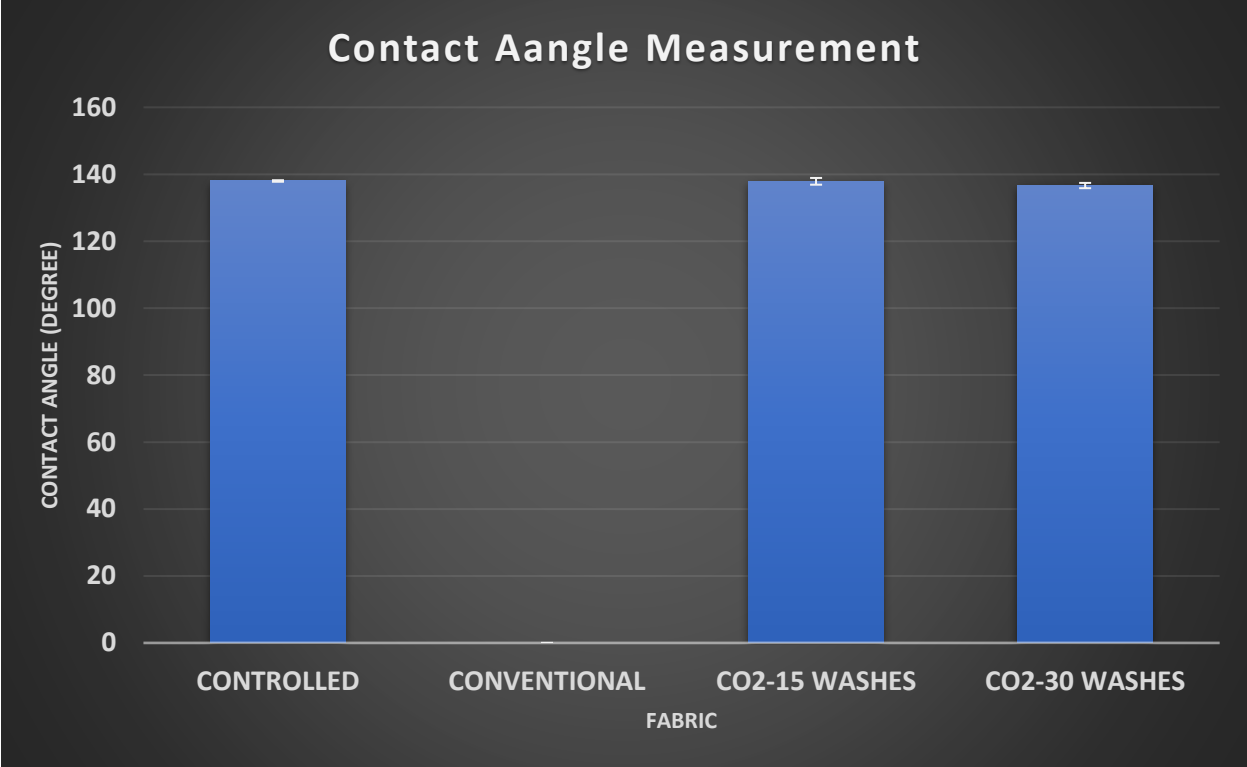


Figure 13-5:Goniometer testing results.

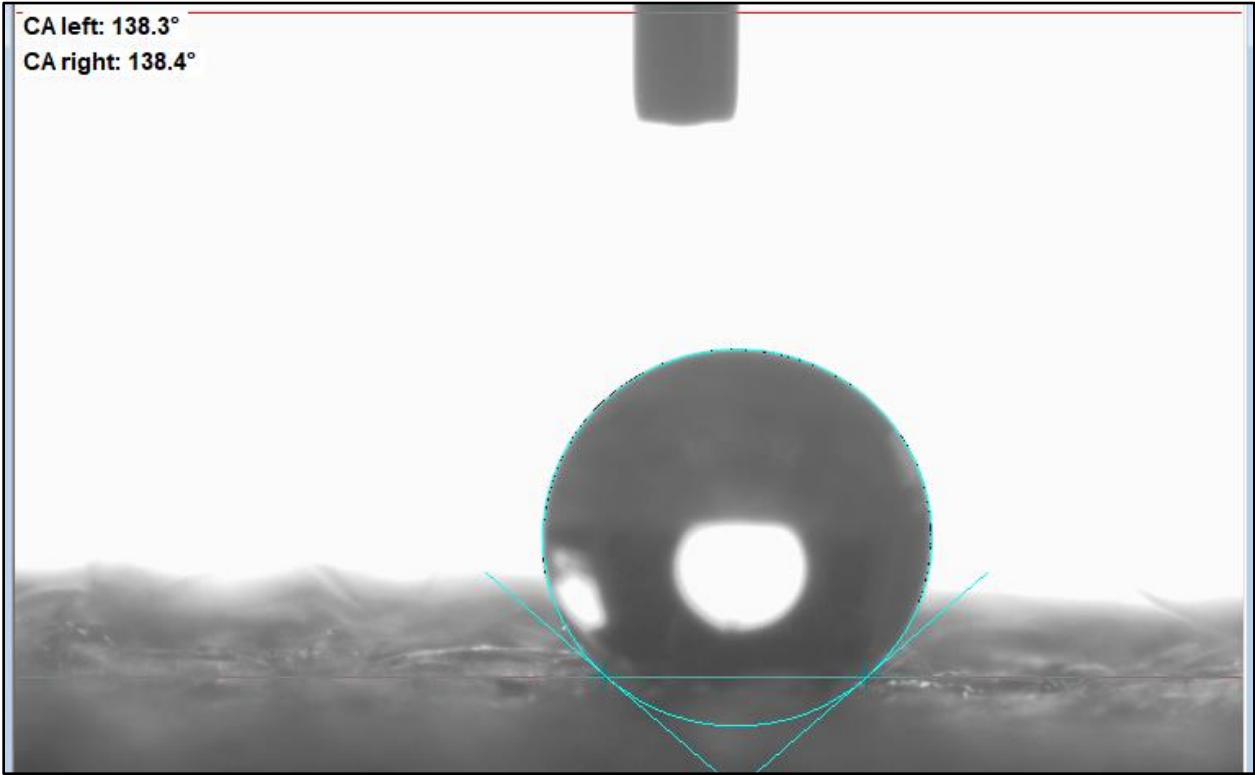
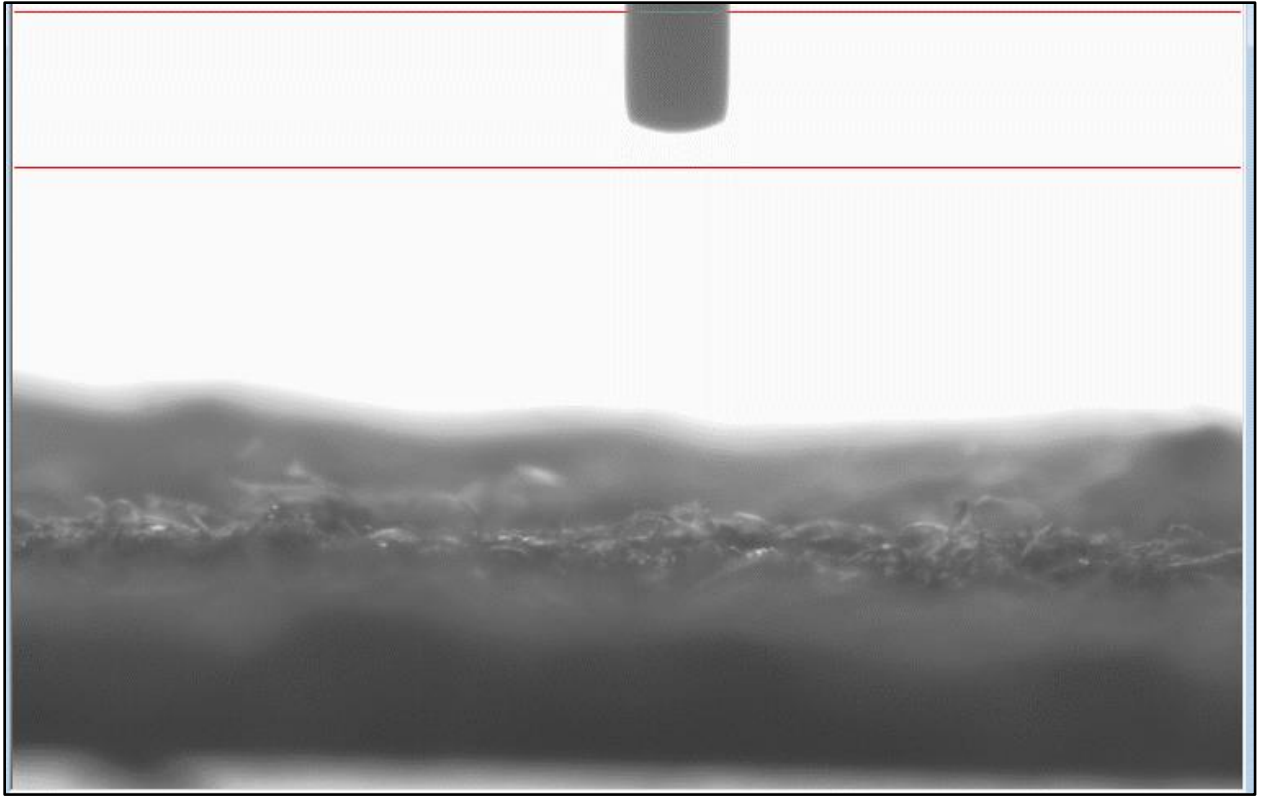
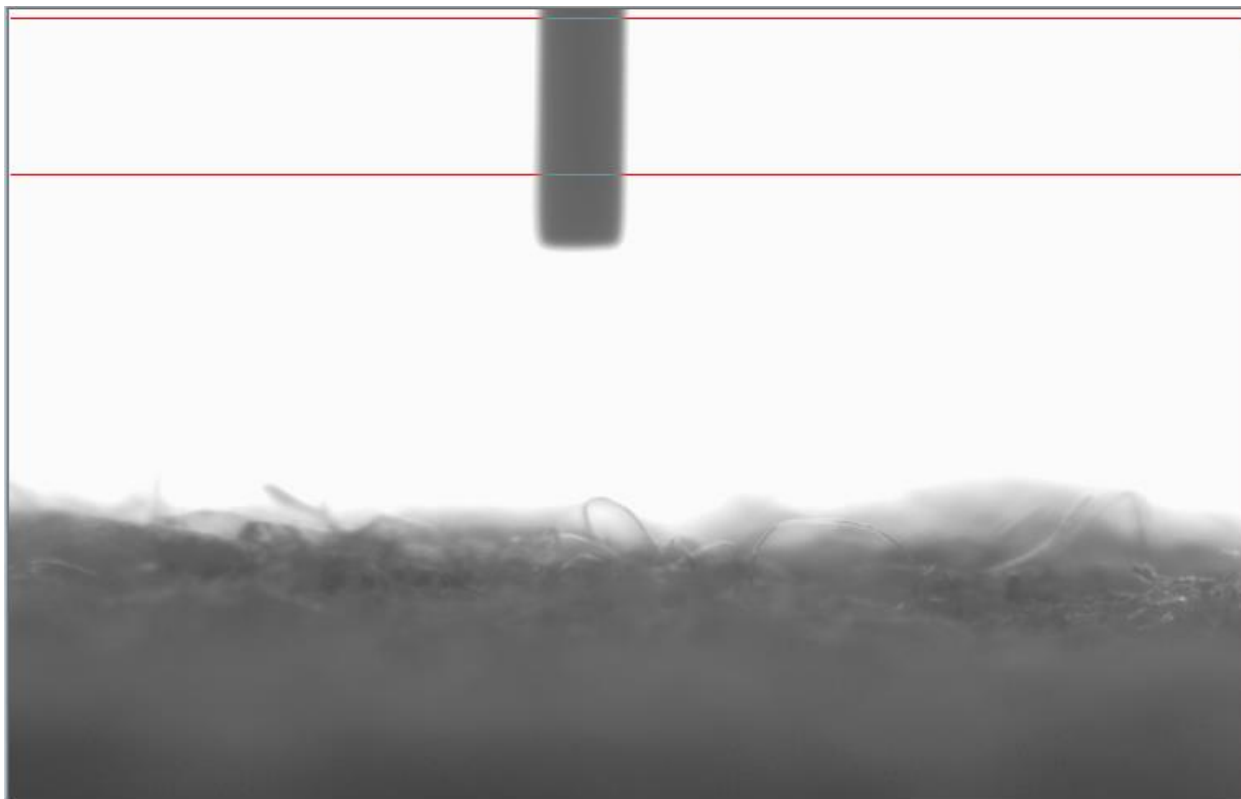


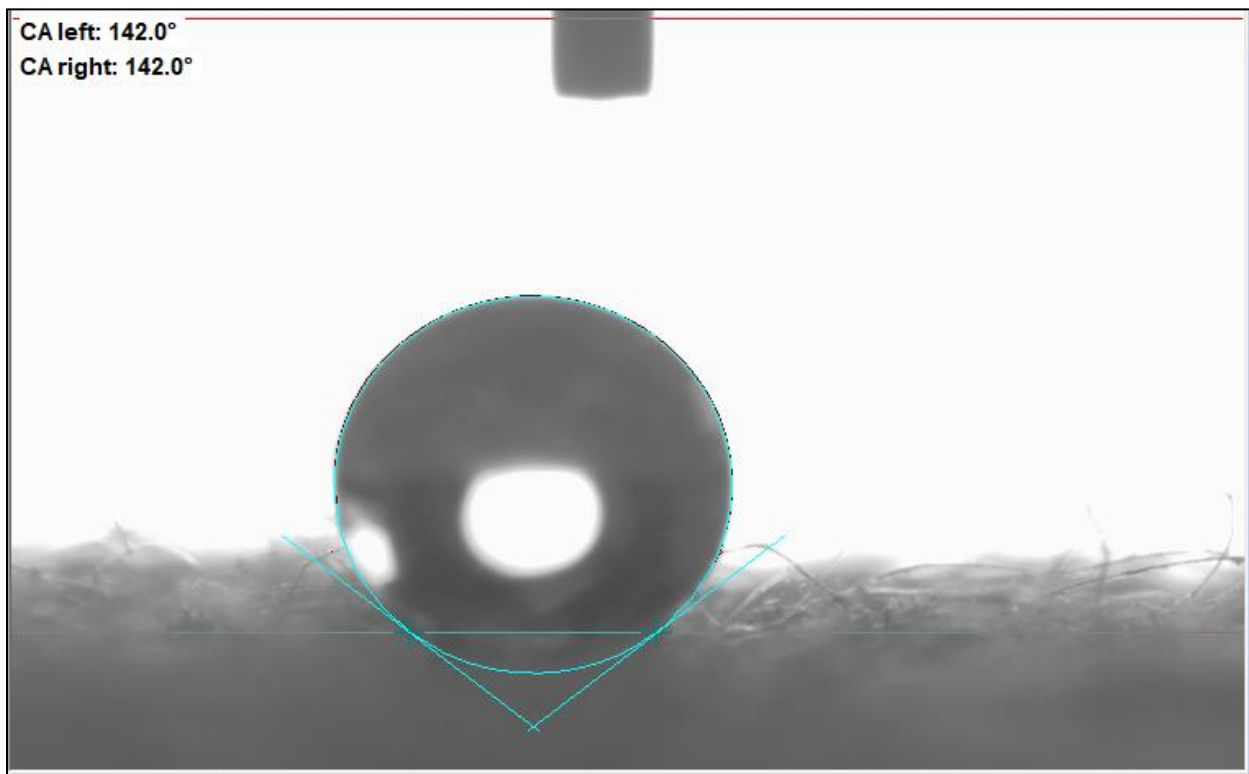
Figure 13-6:Contact angle of the control sample.



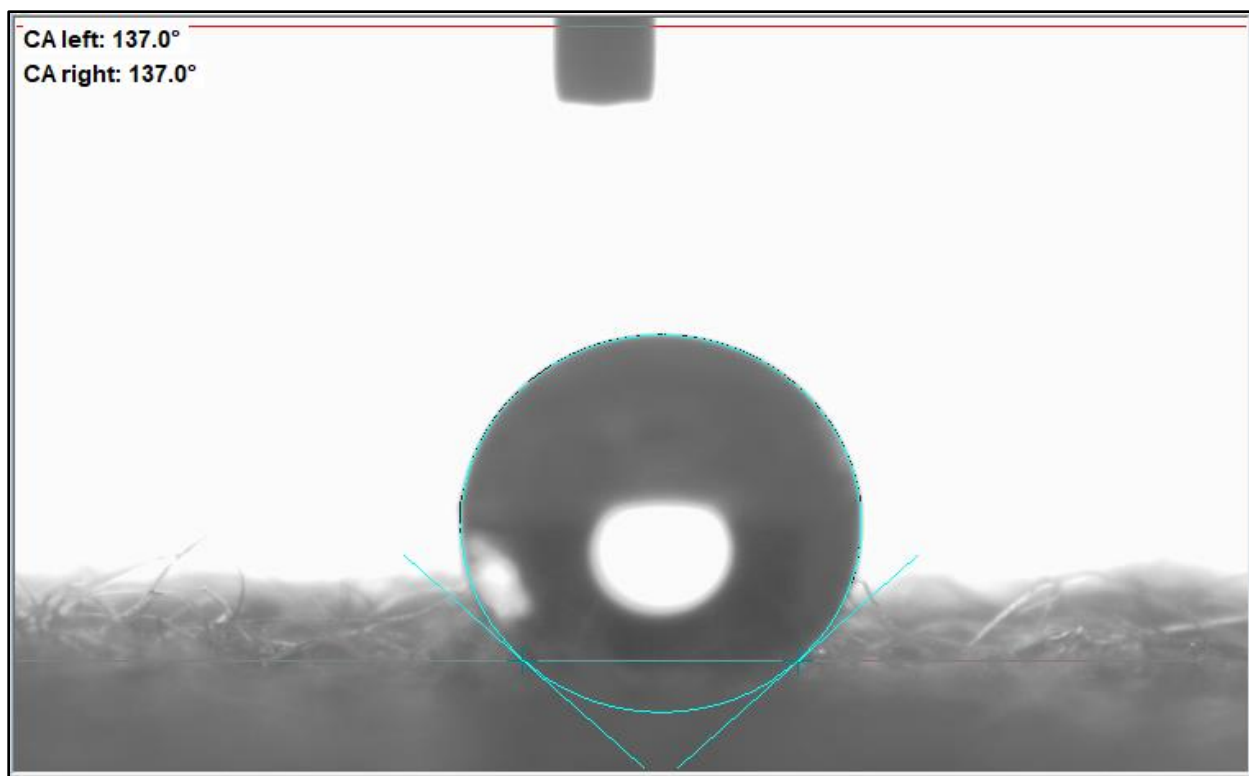
*Figure 13-7:*Contact angle measurement of the conventionally washed fabric.



*Figure 13-8:* Contact angle measurement of the modified wash sample.



*Figure 13-9:* Contact angle measurement of the liquid CO<sub>2</sub>-15 times washed sample.



*Figure 13-10: Contact angle measurement of the liquid CO<sub>2</sub>-30 times washed sample.*

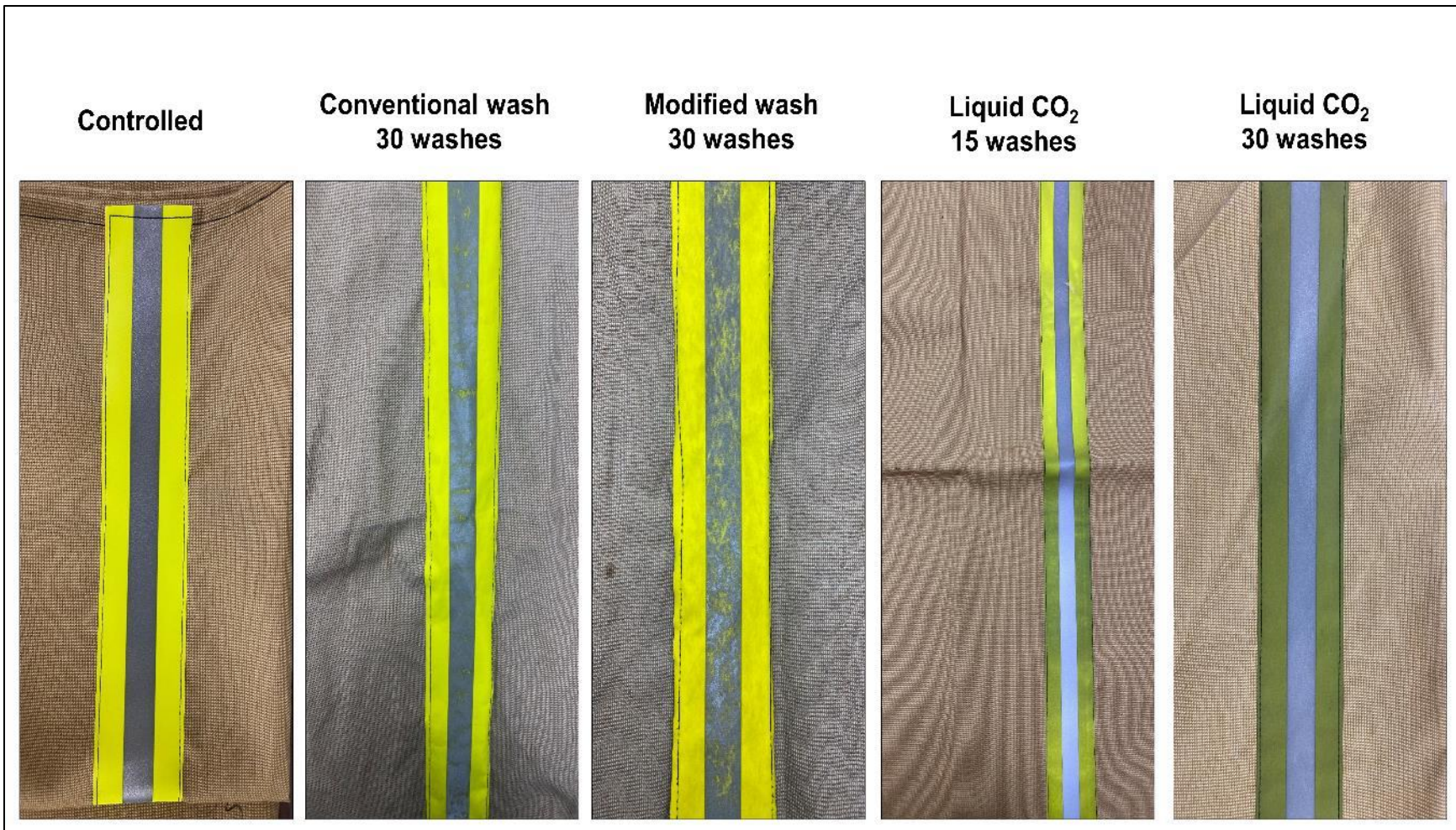
#### *13.3.4 Visual Comparison and Spectrophotometer L\*, a\*, b\* values*

##### *13.3.4.1 Visual Comparison*

The effect of the different washes on the outer shell and reflective trim is shown in Figure 13-11. After 30 washes of the conventional wash method, the color of the outer shell faded and the reflective trim peeled off. The peeling came after the 22nd wash, to be specific. This was a harsh effect of the surfactant exposure for a longer period. There was no damage to the product label due to conventional washing (Figure 13-12). The modified wash had a more severe effect on the reflective trim as more peeling was observed. Along with the surfactant exposure, the higher temperature contributed to this damage. Thus, temperatures as high as 65 °C can damage the accessories of the outer shell material. Out of the four product labels, two of the product labels started to detach from the outer shell garment (Figure 13-13). This was at the end of the

27th washing cycle to be specific. The instructions on the product labels were clear and easy to read for all the product labels. This was true for all the techniques used.

For liquid CO<sub>2</sub> washing, there was no significant color change of the outer shell material. However, the yellow color of the reflective trim was darkened. This might be due to the dissolving of the dye of the trim in the liquid CO<sub>2</sub> while washing. Even for 15 washes, the effect was visible. The whiteness of the product label was also lost somewhat for liquid CO<sub>2</sub> washing.



*Figure 13-11: Visual Comparison of the effect of different washes on outershell and reflective trims-(a) Control (b) Conventional wash (c) Modified wash.*



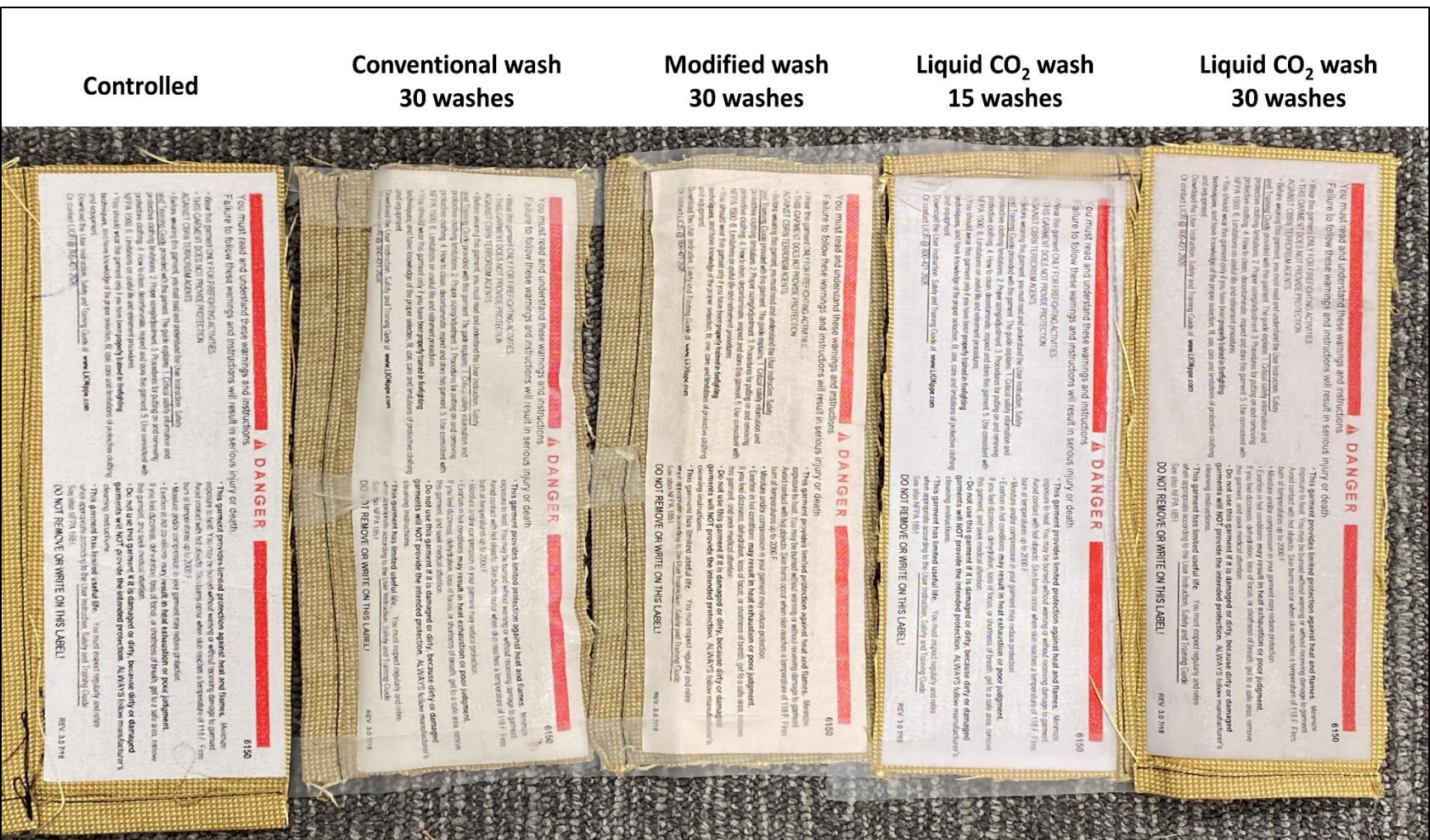
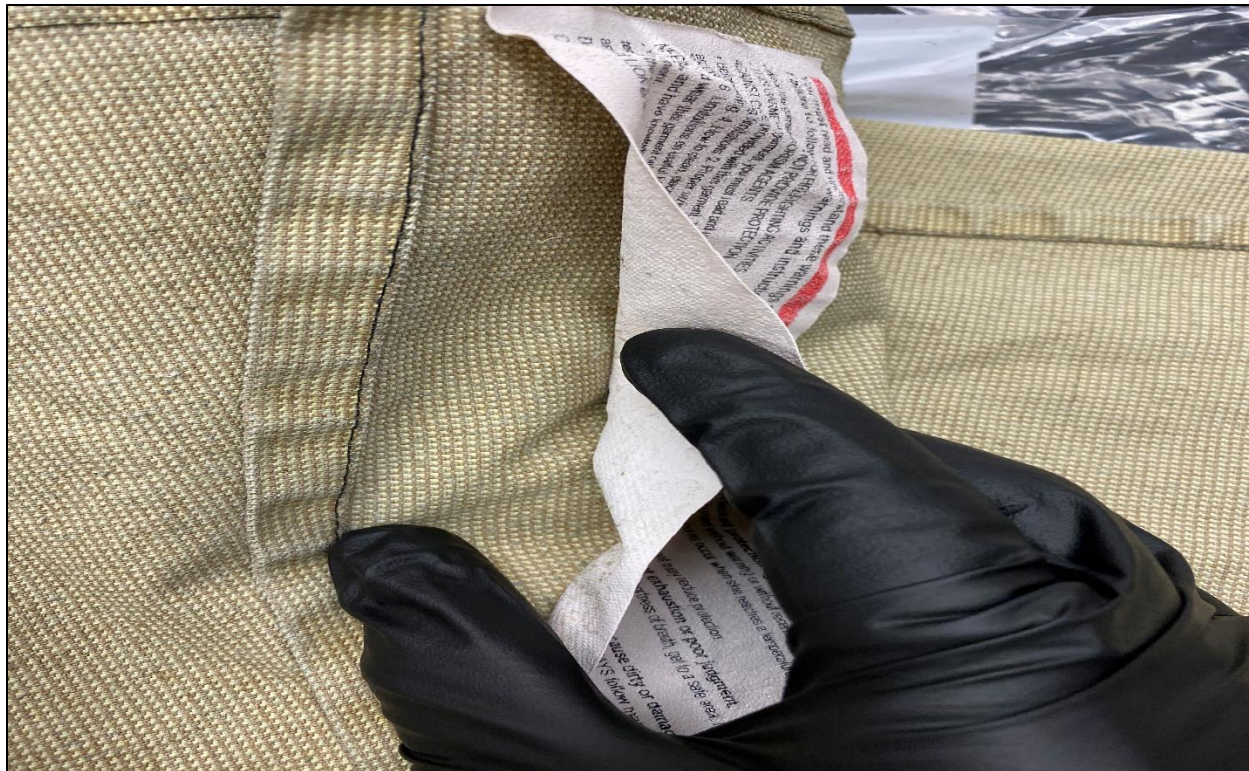


Figure 13-12: Visual Comparison of the product labels.



*Figure 13-13: Product label detaching from the outershell for modified washing.*

#### *13.3.4.2 Color Indices*

##### *13.3.4.2.1 Outer shell*

The color indices comparison is illustrated in Figure 13-14. There was no significant change in the lightness ( $L^*$ ) index of the outer shell materials. The fading of the color of the outershell material was due to a decrease in the blueness of the color as seen from the  $b^*$  values. There was a significant drop in the  $b^*$  values for the fabrics washed with conventional and modified washes. Thus, the yellowness of the fabric increased for aqueous washing. Thus, the surfactants affect the  $b^*$  of the outershell material. The liquid  $\text{CO}_2$  wash did not have any significant impact on the color of the outer shell material.

The delta-E values provided in Figure 13-15 showed that fabrics washed using modified techniques had significant color change followed by conventional washing techniques.

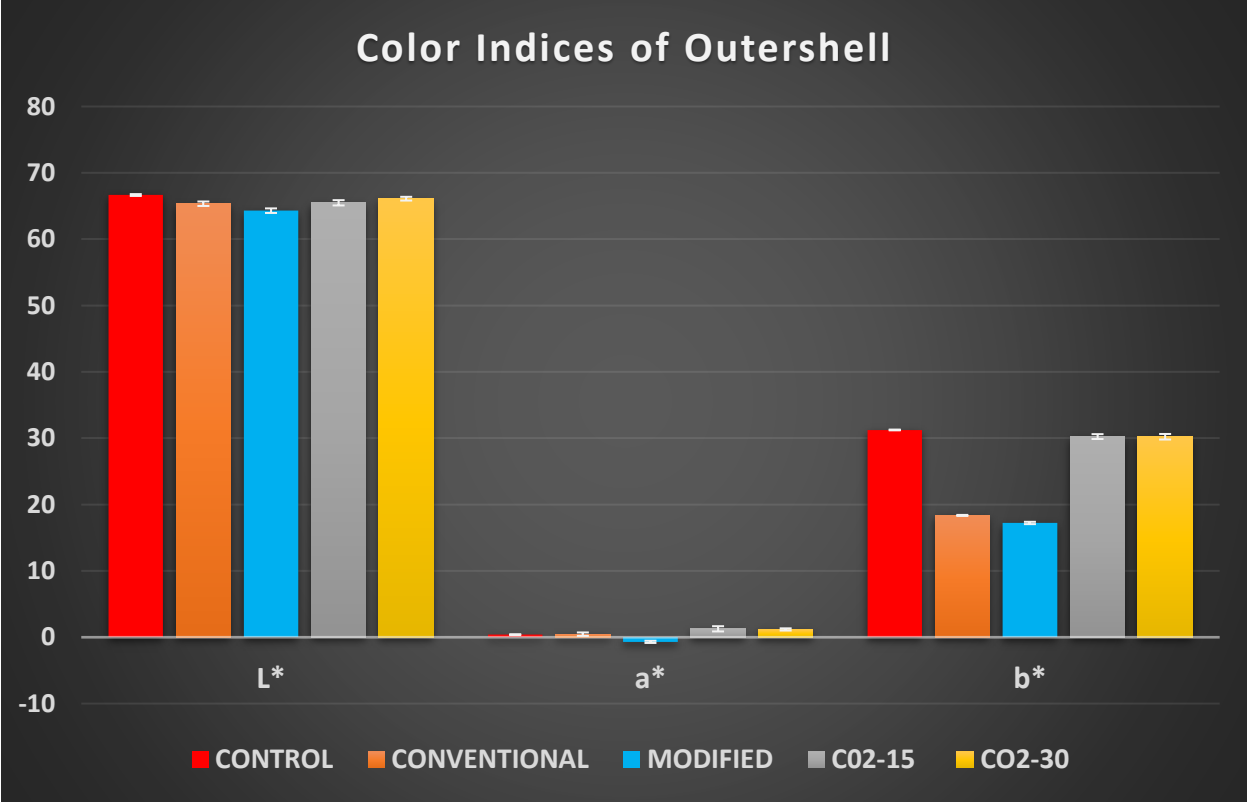


Figure 13-14: Color Indices of the outershell material.

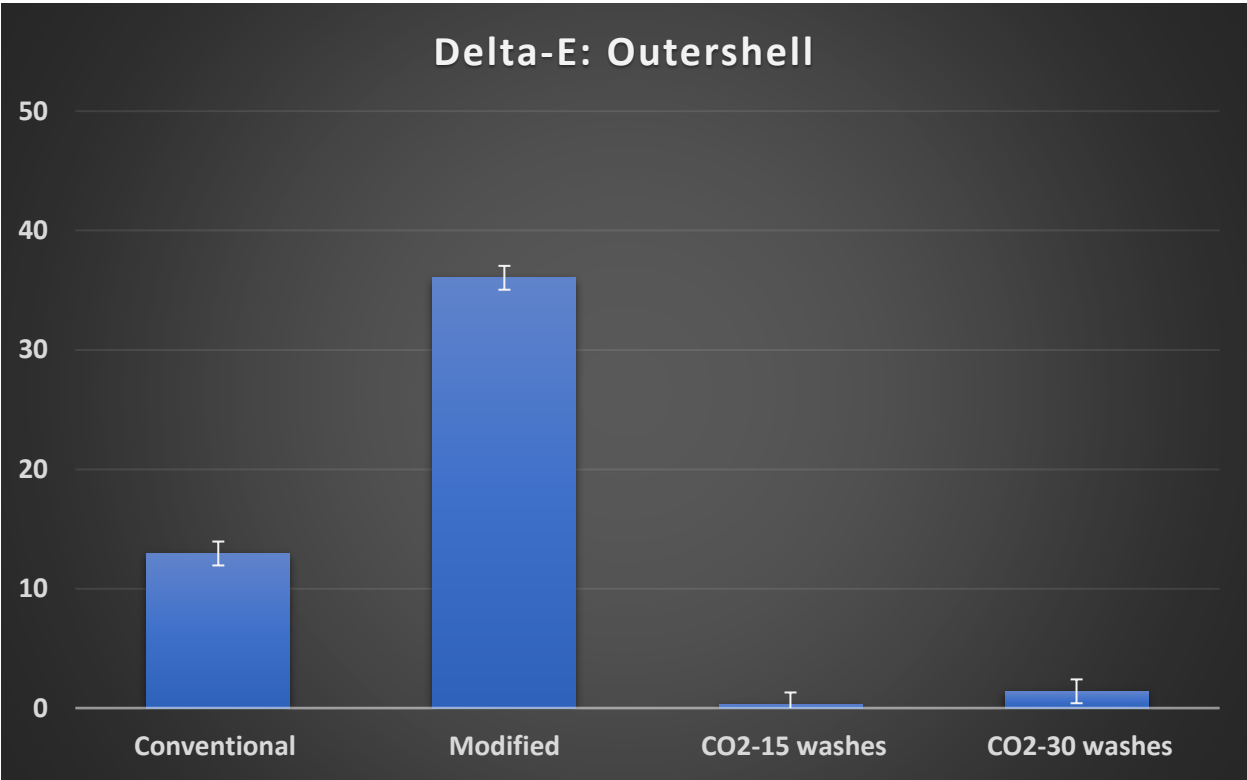


Figure 13-15: Delta-E of the outer shell.

#### 13.3.4.2.2 Reflective trim

The color indices comparison of reflective trim is illustrated in Figure 13-16. The lightness index of the yellow stripe of the reflective trim decreased for all the washing methods. It decreased significantly for the reflective trim washed with liquid CO<sub>2</sub> 15 and 30 times. As seen from Figure 13-11, the yellow color was removed from the trims. When a\* values were compared, the greenness of the reflective trim increased for all the washing methods. The modified wash and liquid CO<sub>2</sub> wash-30 times increased the greenness of the yellow trim. The b\* values were higher for the aqueous washing prominently for the modified washing. This indicated that the blueness of the strip increased for aqueous washing while for liquid CO<sub>2</sub> washing it dropped as the number of washes increased. Thus, the polarity of the solvent affected the yellow strip of the reflective trim. Also, the b\* values were higher as compared to the a\* values, thus indicating that samples became bluer than being red. The delta-E values are shown in Figure 13-17 that shows that liquid CO<sub>2</sub>-30 washes had the highest impact on the yellow stripe of reflective trim. One possible explanation for this is the dye of the reflective trim was dissolved in the liquid CO<sub>2</sub>.

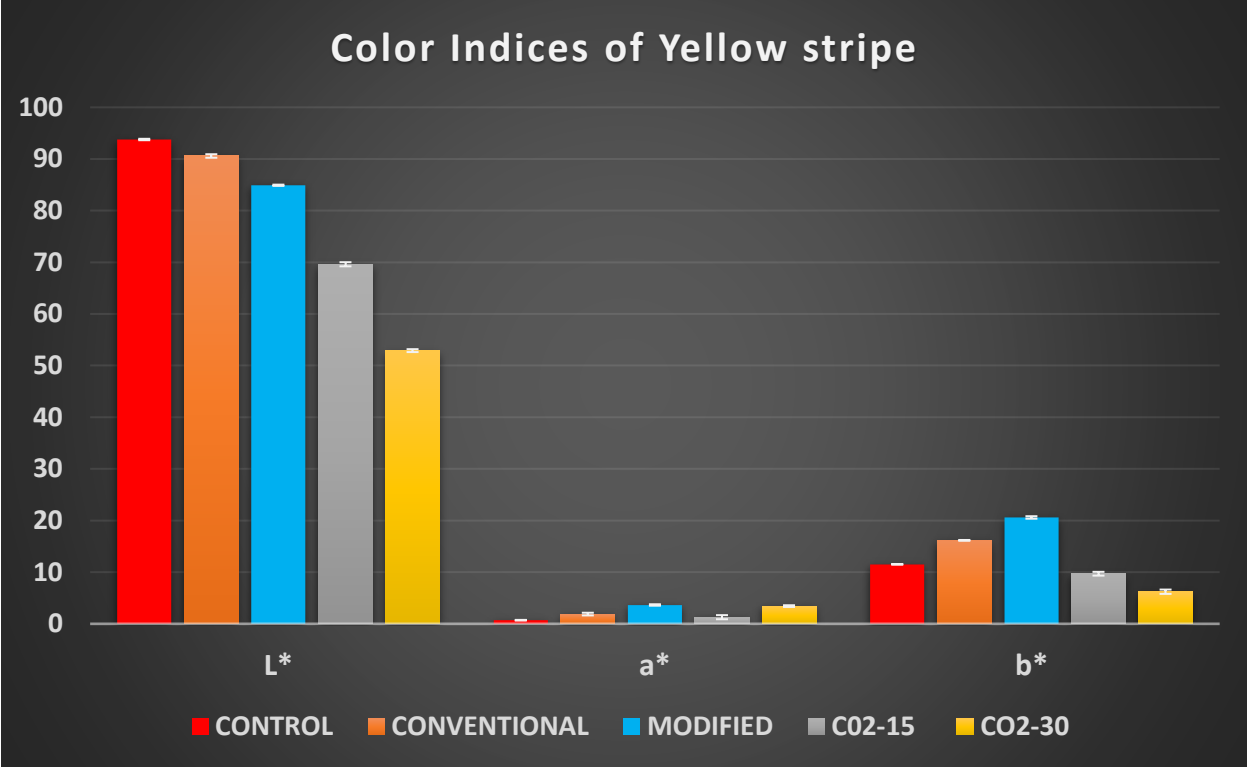


Figure 13-16: Color indices of the yellow strip of reflective trim.

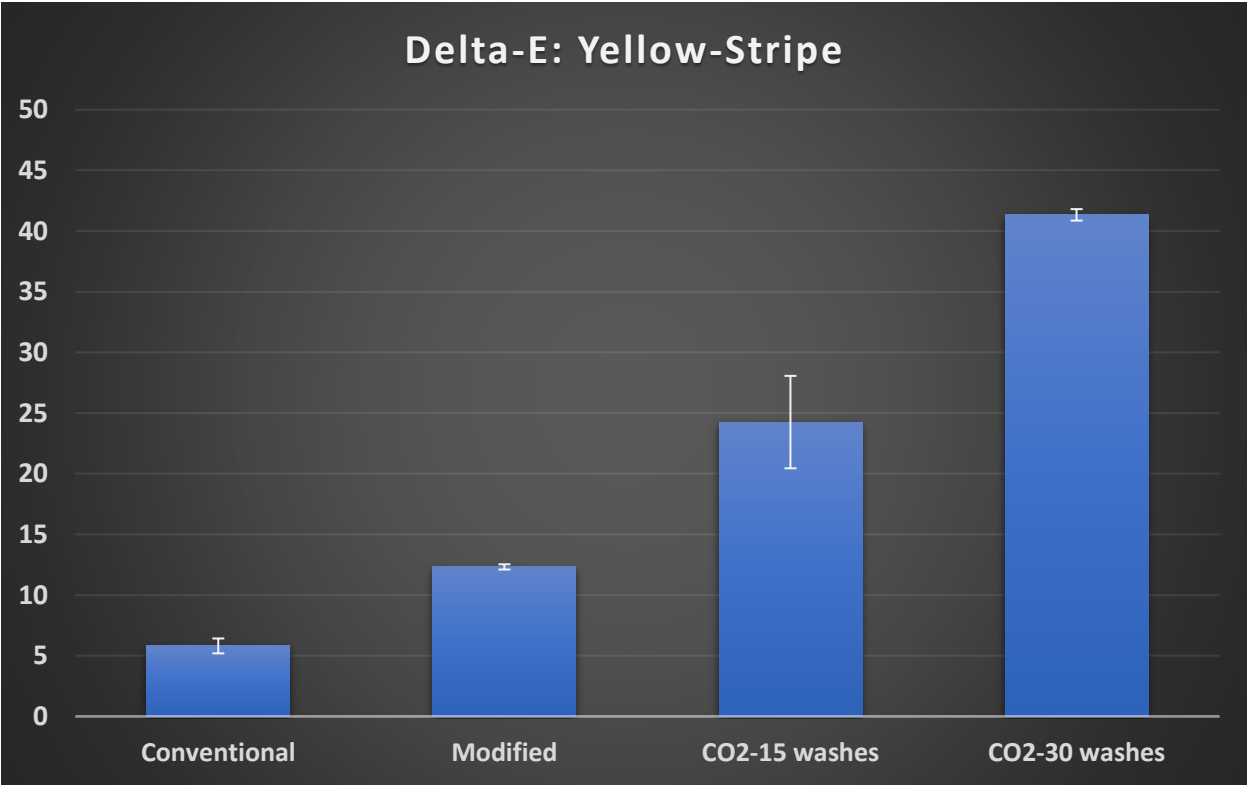


Figure 13-17: Delta-E values for the yellow stripe of reflective trim.

The color indices of the silver strip of reflective trim are shown in Figure 13-18. The lightness index decreased indicating that the stripe was getting darker when subjected to aqueous washing. The values for  $L^*$  for all the samples were comparable. The  $a^*$  values did not have a significant change in color and  $b^*$  values increased for all the washing methods. This indicated that the blue color of the stripe was increasing, and it increased significantly for a modified wash. The comparison of the change in the color of the silver stripe is shown in Figure 13-19 that indicated modified washed samples had a higher color change. The peeling of the reflective trim may have affected the calculations.

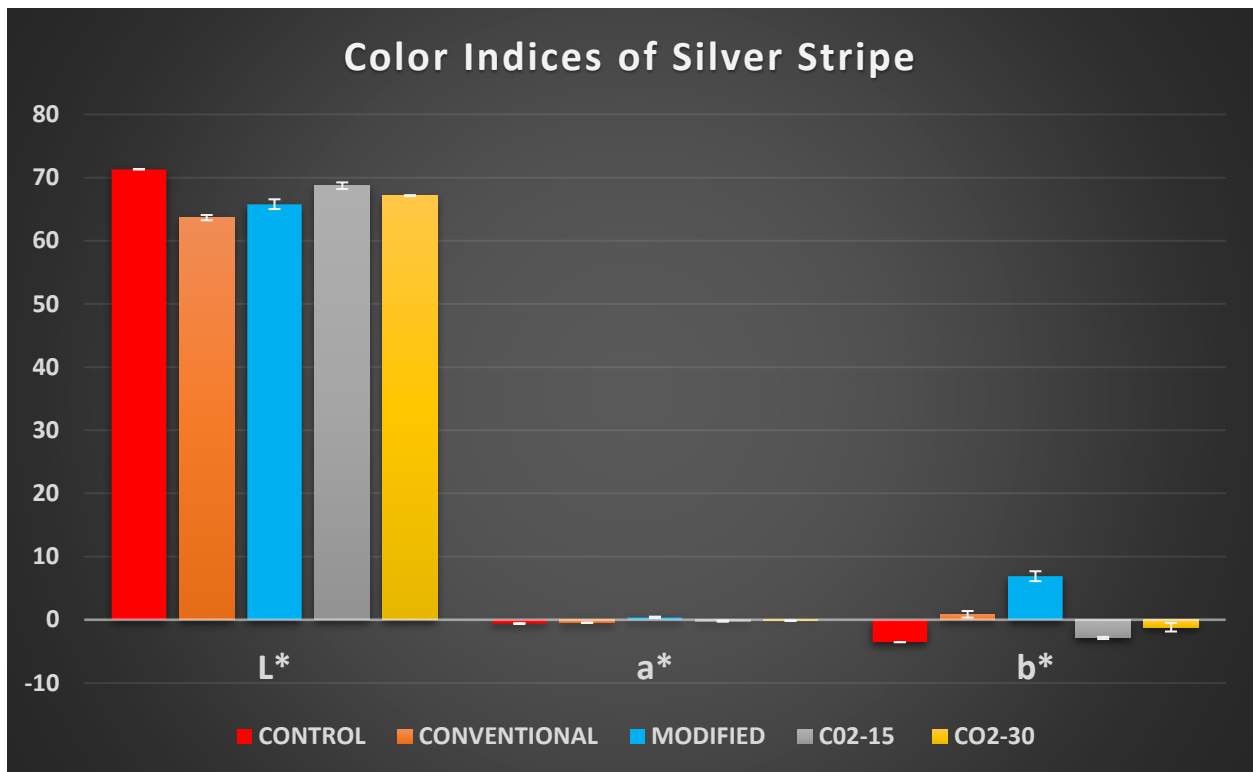


Figure 13-18: Color Indices of the silver strip of reflective trim.

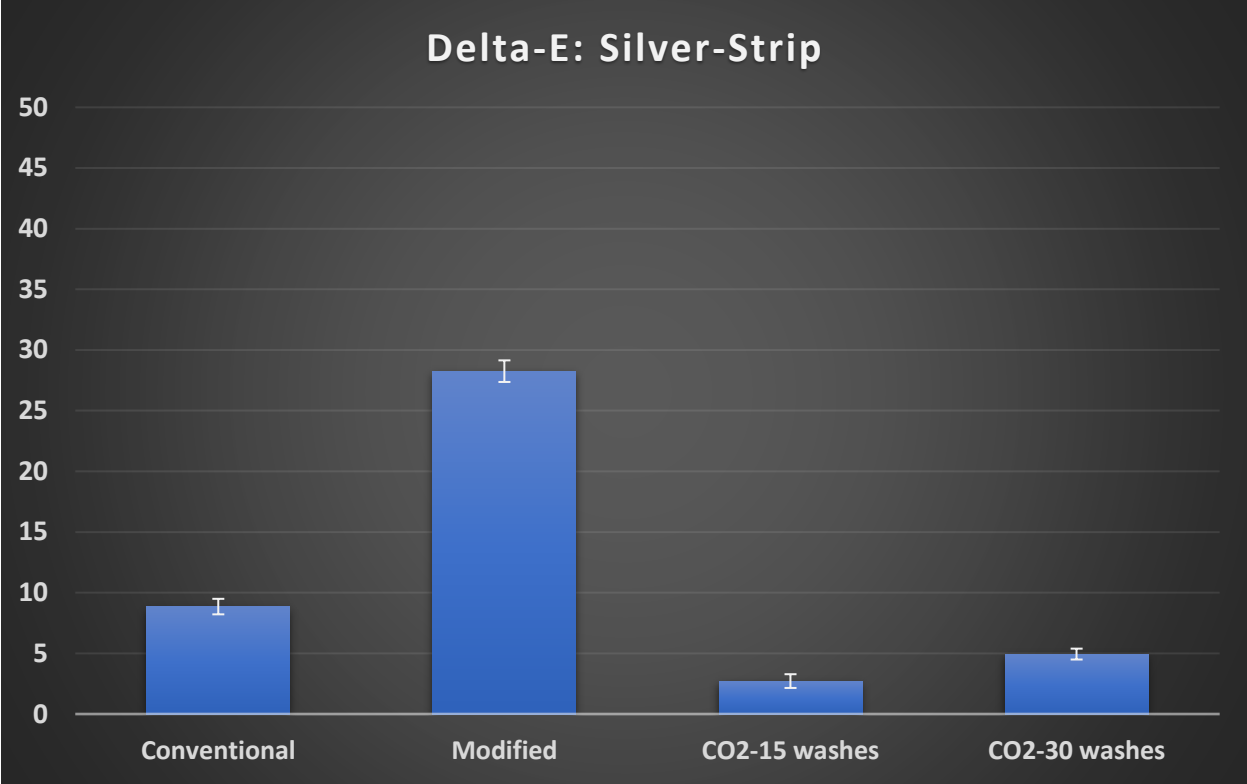


Figure 13-19: Delta-E for the silver stripe of reflective trim.

13.3.4.2.3 Product labels

The lightness index of the product labels is shown in Figure 13-20. The values for conventional wash were comparable which illustrated that the conventional wash did not have any effect on the lightness of the product labels. Higher temperature affected the product label adversely, the lightness index was lost in smaller amounts, and two out of four labels were detached from the outer shell as shown in the previous section. The lightness index of the product labels washed with liquid CO<sub>2</sub> techniques was decreased and there was a decreasing trend as the number of washes increased. The primary reason for this might be that the white dye used in the product label may be dissolved in the liquid CO<sub>2</sub>.

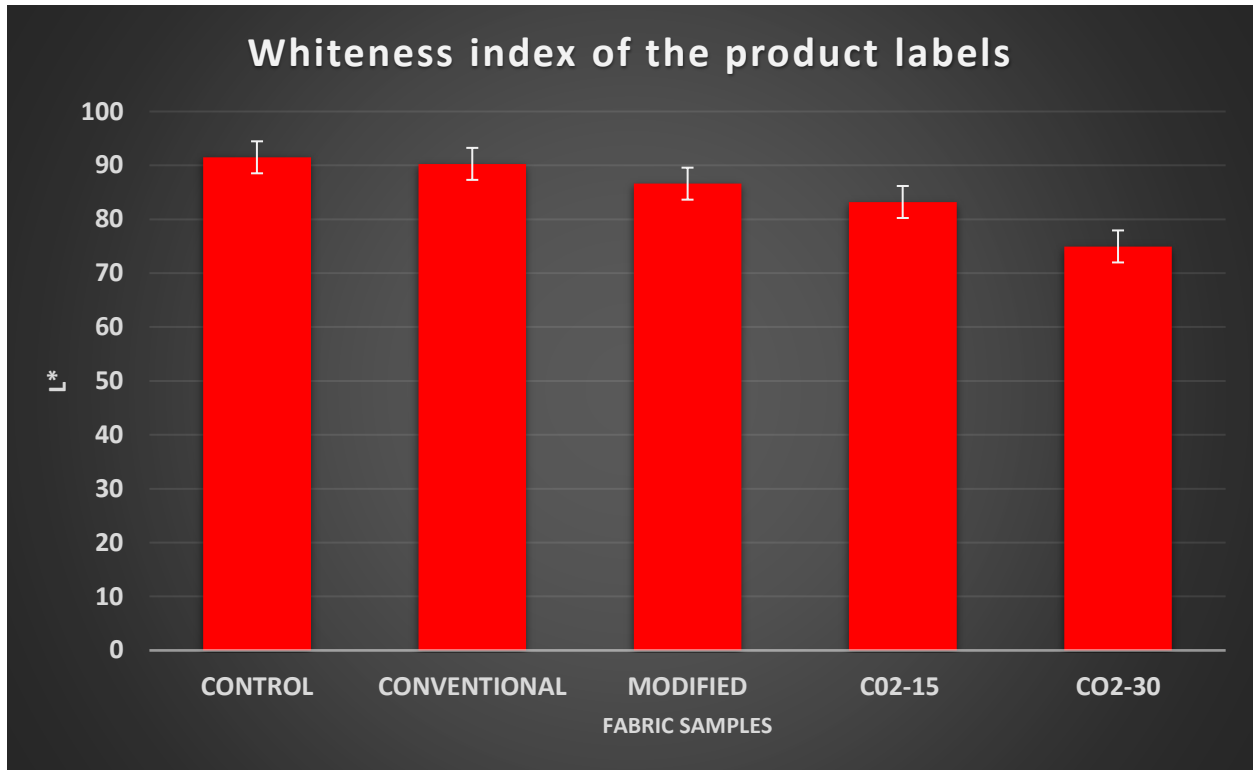


Figure 13-20: Whiteness index of the product labels.

#### 13.4 Conclusion

The durability study of the outer shell and its accessories showed that different washing techniques affect the outer shell and its accessories differently. The conventional wash used in this study was the representation of the effect of the surfactant solution on the garment if used for longer durations. If the duration for the contact of the surfactant solution to the conventional wash is considered on an average as 30 minutes, then every single conventional wash represented in this study can be counted as double. Thus, the conventional wash of 30 times represented washing over 5 years if we consider the turnout suit receive washing once every month. So after 60 washes, the conventional wash can have an impact on the turnout suit and its accessories.

The modified wash represented here used commercial detergent with the recommended quantity. The study showed the effects of higher temperature on the turnout suits and their



accessories. The breaking, tearing strength, and hydrophobicity of the outer shell material was lost after 30 washes of the modified washing technique. This could happen when it is washed frequently at higher temperatures. Hence, further investigation of the optimization of the number of washes, higher optimized temperature and its effects need to be studied.

The liquid CO<sub>2</sub> washing technique used in this study showed that it did not have any significant effect on the tearing strength, breaking strength, the water repellent finish applied on the outer shell material. However, it had an impact on the reflective trim and product labels. This was the only drawback of the liquid CO<sub>2</sub> technique. The effect was also seen on 15 washes. If the liquid CO<sub>2</sub> technique is used once every six months then 15 washes represent washing over seven and half years which is approximately equivalent to 75% of the life time of a turnout suit used in service i.e. ten years.

One interesting conclusion was different washing techniques affect different combinations of color indices of the outer shell material and its accessories. An important point to ponder is the entire study was performed on one type of outer shell, reflective trim, product label. A study comprising a variety of outer shell materials and accessories from different manufacturers needs to be completed to gain a more comprehensive understanding of the effects of different washing techniques on the turnout suits. A similar approach needs to be taken for testing the effects on the inner layers as well.

## Chapter 14: Conclusion and Scope of Future work

### 14.1 *Conclusion*

The current studies were focused on understanding the effect of various parameters on the contaminant removal from the turnout suit. This helped in understanding the fundamental aspect of the cleaning procedures. One of the objectives of the research was to develop a bench-scale washing method which was successfully achieved. The bench-scale washing procedure developed in this research provided a relatively quick and simple evaluation of the washing efficiency of surfactants and washing parameters. The evaluation of the current washing procedures (when washed with parameters according to the NFPA 1851) on a bench scale demonstrated its efficacy in a controlled environment. The author and his team were able to fill up a major research gap by evaluating the effects of washing parameters on washing efficiency in a controlled environment. The design of experiments for the bench scale showed that the nature of the contaminants varies considerably thus highlighting the importance of the chemistry of the surfactants with the contaminants. Also, the study using statistical data modeling showed that the decontamination of the suits is a problem with no one solution. Phenols and simple PAHs are removed effectively with aqueous washing. The hydrophobic nature of the larger PAHs and phthalates hindered their removal from the fabric. The study highlighted that to remove the contaminants effectively there is a need for better surfactants.

The comparative analysis of the full-scale washing with bench-scale indicated that the bench-scale level and full-scale level wash predicted a similar trend for chemical classes. The redeposition of the contaminants can impede the evaluation of the washing efficiency. The common conclusion across all the studies was the inverse relation of the washing efficiency of a compound with its  $K_{OW}$  value. Both washing studies showed that the surfactant is an important

parameter in removing the contaminants and temperature and time are parameters that further aid in removing the contaminants. Of the three classes, phthalates were the most difficult to be removed during both bench-scale and full-scale washing. Briefly explained, there is a limited scope in the removal of phthalates using the current surfactants.

The bench-scale testing of different surfactants demonstrated that the method developed can be used in screening surfactants. The microbial surfactant used in the study did not provide any distinct advantage over the commercial surfactants. The second set of surfactants provided by a different manufacturer when tested on the bench scale demonstrated a high level of contaminant removal, especially for BaP and DEHP. However, the high volume of the surfactant used may have contributed to that. Such a high volume of surfactant can damage the turnout suits as seen in the Broward County gear study. The bench-scale study of modified surfactants concluded that there is a potential in removing complex PAHs and phthalates more effectively by modifying the surfactants.

The investigation of the liquid CO<sub>2</sub> technique showed that the technique worked effectively in removing overall contamination in a controlled study. The results were statistically significant when compared with conventional wash. The high pressure and non-polar nature of liquid CO<sub>2</sub> worked in favor of the desorption of phthalates and BaP from the fabric surface. The technique did not have any adverse effect on the outer shell garment's physical properties when washed multiple times. However, there was a darkening of the color of the reflective trim and product label.

The real-world sample studies showed that contamination of the turnout suits is a very complex phenomenon. Phthalates were the only targeted compounds detected in the garments. PAHs and phenols were not detected in any of the evaluated turnout suits. When assumed that

the turnout suits, received on-scene decontamination and regular washing in a washing machine, the conclusion was phthalates were stubborn contaminants that persist in both the decontamination techniques while on-scene decontamination may have significantly removed PAHs since they were more likely to be adsorbed on the particulates from the smoke. Thus, an on-scene decontamination study is warranted. The spatial variability of the contaminant on the garment was very high. This made the evaluation of the washing efficiencies of different techniques very difficult. Overall liquid CO<sub>2</sub> worked better as compared to the conventional technique. Although when average washing efficiency for real-world samples is compared with controlled study for liquid CO<sub>2</sub> technique, the contamination decreased for all the phthalates. The deviation in the results may be attributed to the fact that for real-world samples there is particulate contamination and liquid CO<sub>2</sub> has low particulate removal. Thus, mechanical agitation may be needed to improve the washing efficiency of the technique. The absence of polarity in liquid CO<sub>2</sub> cleaning is a primary reason that the particulates can redeposit. For the Broward County gears study, liquid CO<sub>2</sub> showed higher cleaning efficiency when compared to conventional wash. The modified washing technique for this study included high-temperature washing and a high volume of surfactants. This demonstrated the extreme case of the parameters, and it affected the turnout suits adversely. Thus, showing the negative impacts of the upper levels of washing parameters.

The durability studies showed that any washing technique over time can affect the turnout suit. The conventional washing affected the tearing strength of the outer shell and the peeling of the reflective trim. The contact angle measurement showed that the conventional wash and modified wash both completely removed the water repellent finish. It showed the impact of

prolonged exposure to surfactant solution. Modified washing technique demonstrated that higher temperatures such as 65°C can damage the gear adversely.

In conclusion, the conventional washing technique has limits in removing phthalates and complex PAHs such as pyrene and BaP. Compounds such as BaP, pyrene, DEHP, BBP require higher pressure and specialized cleaning to be removed from the fabric. The amount that is removed from the fabric using conventional washing may be the maximum that can be achieved and if the remaining compounds are not readily released from the material at ambient conditions, the question of whether the residual amounts of contamination pose a threat to the health of firefighters could be asked?

For outer shell material, specialized cleaning such as liquid CO<sub>2</sub> can help in improving the decontamination. Hence, based on the research finding, the liquid CO<sub>2</sub> technique can be incorporated as specialized cleaning and the turnout suits can receive the washing quarterly or semi-annually.

#### 14.2 *Future Work*

The current study is performed entirely on the outer shell material only. The bench-scale washing method demonstrated evaluation of the washing procedure in a controlled environment. This study can be modified to incorporate another swatch of the same size that is uncontaminated and put it in the same beaker as the contaminated swatch to understand the redeposition of the contaminants. The redeposition percentage can help in evaluating the washing efficiency of the garment more thoroughly. Similar incorporation can be done on the garment at full-scale washing to see the results. This will help in understanding the efficacy of the surfactant on a full scale. The comparative analysis will give a better understanding of the similarities and differences between bench-scale and full-scale approaches. Modifications of surfactants need to

include incorporating non-polar compounds, additives like activated carbon, guar-gum, and microbes to improve the potency of the surfactant.

The author presented a concept of higher washing temperature (65°C). A further investigation of washing at a median temperature such as 50°C needs to be executed to find an optimized temperature for washing and then study its effect on the durability of the turnout suits. An investigation of the incorporation of the effect of higher pressure on washing efficiency needs to be performed. The liquid CO<sub>2</sub> technique showed high removal efficiency for the outer shell material. A separate comparative study needs to be conducted on the inner layers to evaluate its efficiency. The moisture barrier and thermal liner are delicate layers of the PPE hence the impact of liquid CO<sub>2</sub> on the durability of these layers should also be studied. The wettability test showed that liquid CO<sub>2</sub> did not have any significant impact on the water repellent finish but testing for hydraulic fluid needs to be conducted to assess oil repellency.

An interesting conclusion that came out of the legacy gear assessment was the effect of gross decontamination or on-scene decontamination on the turnout suit can be more significant than expected. Since the brushing of the particulates from the turnout suits can decrease the probability of residual contamination such as BaP and pyrene that partition more towards particulates from the smoke. The evaluation of on-scene decontamination will provide us with solutions to reduce the residual contamination and ultimately reduce the health hazards to the firefighters.

The research showed that after conventional washing, residual contaminants were present in certain amounts. Even modified washing such as higher temperature did not remove compounds such as BaP or DEHP. Specialized cleaning such as liquid CO<sub>2</sub> incorporates high pressure to squeeze out the contaminants from the fabric. Even after specialized cleaning, if the

residual contamination persists then the following question is raised: what if the amount of contaminant that is removed from the fabric is the maximum amount that can be removed? If yes, then a separate risk assessment needs to be conducted to investigate whether the residual contamination can affect the health of the turnout suits in daily life when normal conditions are present for example, room temperature, atmospheric pressure, relative humidity, etc.

The durability study on the outer shell and its accessories from different manufacturers needs to be conducted to understand the effects of multiple washing of different techniques on the life cycle of the turnout suits.

**Disclaimer:** *The author and the TPACC labs are not promoting any product or a particular institution. Only results are presented here.*

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