Retention of Odorous Compounds by Textile Materials

by

Mohammed Mukhtar Abdul-Bari

A thesis submitted in partial fulfilment of the requirements for the degree of

Master of Science

in

Textiles and Clothing

Department of Human Ecology
University of Alberta

Abstract

Body odour consists of different compounds that interact in various ways with textile materials due to differences in their chemical properties. Clothing made from hydrophilic fibres (e.g., cotton) can be more easily laundered, and odorants more effectively removed than those made from hydrophobic fibres (e.g., polyester). Therefore, the purpose of this research was to examine the interactions between textile materials and odorous compounds when washed several times with different detergents. Test fabrics were of both interlock knit structure and either 100% cotton (234 g/m^2) or 100% polyester (224 g/m^2) fibre content. Test compounds were 4-ethyl octanoic acid (octanoic acid) and 2-nonenal (nonenal). Fabric samples were spiked with 10 μL of a solution of octanoic acid (0.1g), nonenal (0.1g) and dichloromethane (solvent) and left to sit for 24 hours. Inoculated samples were washed with either Tide® Free and Gentle detergent or Tide® Febreze Sports detergent. Residual odorants were measured using gas chromatography with flame ionization detector. Headspace analysis of volatiles was conducted using solid-phase micro-extraction (SPME); direct extraction of compounds remaining in fabrics was done using dichloromethane as the solvent. Considering the peak area of odorants, findings show that cotton generally retained and desorbed lesser odorous compounds than polyester did. Interestingly, the non-polar nonenal was difficult to remove from the non-polar hydrophobic polyester by washing, which resulted in higher quantities of nonenal compared with octanoic acid in the headspace. Also, while multiple washes eventually became more efficient in removing odorants from cotton, polyester did not clean as well.

Preface

This thesis is an original work by Mohammed Mukhtar Abdul-Bari. No part of this thesis has been previously published.

Acknowledgements

I would like to express my sincere gratitude to my supervisor, Dr. Rachel McQueen for the extra funding, for her patience, motivation and guidance throughout the research and writing of this thesis. Dr. McQueen is an embodiment of an ideal mentor and I am fortunate to have been her mentee. The bicycle gesture left an indelible impression on my friends and me.

As well as my supervisor, I would like to thank the rest of my supervisory thesis committee Dr. James Harynuk and Dr. Paulina De la Mata, for their extensive professional guidance and for teaching me a great deal about scientific research.

Thanks to Dr Williamson, her staff and the entire student body, the Department of Human Ecology has been a home to me. I am also genuinely thankful to McQueen’s Group (Mariko, Sara and Lauren) who took most of our research workload, which allowed me to have more time for my thesis. To Harynuk’s Group, I am grateful for your patience in training and support during my thesis and related projects. Special thanks to Dr. Nancy Kerr, Robin, Keisean and Gasser, for their insights into understanding and explaining my results.

Mary, Anne, Farzan and my many friends; your genuine friendship and support was appreciated more than I can express. The opportunity for this experience was made possible through Dr. Jane Batcheller’s acceptance of my application on behalf of Dr. McQueen. Thank you for being there for me as another supervisor; you opened the door for this memorable experience.

Financial support was provided by: Dr. Rachel McQueen; Graduate Research and Teaching Assistantships from the Department of Human Ecology; Helen DeSilva Buchanan Memorial Graduate Scholarship; Natural Sciences and Research Council (NSERC) of Canada; and Cotton Incorporated for kindly supplying fabrics for the experiments.

My profound gratitude goes to my family, especially my parents and Kamil for their constant inspiration and support during this degree as well as all aspects of my life. To Sadik and Effon families, thank you for the trust, confidence and for going above and beyond to see me come this far.

Finally and most importantly, I give thanks to Allah for making this happen the way it did.

Table of contents

Chapter 1 1

Introduction 1

1.1 Background 1
1.2 Statement of problem and purpose 3
1.2.1 Statement of problem 3
1.2.2 Purpose 3
1.3 Objectives 4

Chapter 2 5

Review of Literature 5

2.1 Development of body odour 5
2.1.1 Sweat and sebum 5
2.1.3 Odorous compounds 6
2.2 Textile fibres and fabrics 9
2.2.1 Cotton and polyester fibres 9
2.2.2 Interaction of textiles with body odour 12
2.2.3 Interaction between sweat and bacteria in textile materials 13
2.3 Laundering to remove odours from clothing 14
2.3.1 Detergency 15
2.3.3 Soiling and build-up of odour 19

Chapter 3 22

Methods 22

3.1 Experimental design 22
3.2 Materials and chemicals 22
3.2.1 Experimental fabrics 22
3.2.2 Chemical compounds 25
3.1.3 Laundering 27
3.2.4 Inoculation/wash cycles 32
3.2.5 Headspace analysis using Solid Phase Micro-Extraction Fibre (SPME) 32
3.3 Data analysis 36
3.3.1 Statistical analysis 39

3.4 Preliminary testing 39
3.4.1 Retention times 39
3.4.2 Storage 40
Chapter 4 42

Results 42

4.1 Initial sorption of odorants in cotton and polyester fabrics 42
4.2 Reduction in odorous compounds following one wash 42
4.3 Comparison of fabrics in the direct extraction of octanoic acid and nonenal 46
4.4 Comparison of fabrics in headspace sampling of octanoic acid and nonenal 51
Chapter 5 56

Discussion 56

5.1 Initial sorption of odorous compounds in unwashed fabrics 56
5.1.1 Direct extraction of compounds from fabrics 56
5.1.2 Headspace analysis of compounds emitted from fabrics 56
5.2 Effect of laundering on the removal of odorants from fabrics 59
5.2.1 Fibre interactions with compounds 59
5.2.2 Effect on inoculation/wash cycles on removal of odorants from fabrics 60
5.2.3 Effect of detergents on removal of odorants 62
Chapter 6 64

Summary, conclusions and recommendations 64

6.1 Summary 64
6.2 Conclusions 65
6.3 Recommendations 66
References 68

Appendix A 82

Appendix B 83

Laundering equipment and test parameters. 83
Appendix C 85

Calibration of standard solution 85

List of tables

Table 3.1 A 2 x 2 x 2 x 3 factorial design: 2 odorous compounds x 2 fabrics x 2 detergents x 3 wash levels 23
Table 3.2 Experimental materials........ 24
Table 3.3 Retention time for compounds separately and in solution (with other odorants) 41
Table 4.1 Peak area of octanoic acid and nonenal for head-space sampling and direct extraction (with dichloromethane) from cotton and polyester fabrics following washing. 44
Table 4.2 Significance of variables affecting direct extraction of octanoic acid - ANOVA ($\log_{10}$ transformed) 48
Table 4.3 Significant differences of variables direct extraction of octanoic acid from fabrics. .. 48
Tukey range tests 48
Table 4.4 Significance of variables affecting direct extraction of nonenal from cotton and polyester- ANOVA ($\log_{10}$ transformed) 50
Table 4.5 Significant differences of variables direct extraction of nonenal from polyester (Tukey range tests) 50
Table 4.6 Significance of variables affecting headspace sampling of octanoic acid - ANOVA ($\log_{10}$ transformed) 53
Table 4.7 Significant difference variables affecting the headspace sampling of octanoic acid on fabrics. (Tukey range tests) 53
Table 4.8 Significance of variables affecting headspace sampling of nonenal from cotton and polyester- ANOVA ($\log_{10}$ transformed) 55
Table 4.9 Significant differences of variables affecting headspace sampling of nonenal from polyester (Tukey range tests) 55
Table C1 Calculations for concentrations (ppm) of octanoic acid and the resultant peak areas for calibration curve 86
Table C2 Calculations for concentrations (ppm) of nonenal and the resultant peak areas for calibration curve 87

List of figures

Figure 2.1 Chemical structure of the cotton fibre (Designed using ChemDraw®) 10

Figure 2.2 Chemical structure of polyester fibre, $R_1 = CH_2\text{-}CH_2$; R_2 = Benzene ring (Designed using ChemDraw®) 11

Figure 2.3 Structure of a surfactant.. 15

Figure 3.1 Fabric samples laid in Petri dishes 26

Figure 3.2 A wash stock solution with a siphoning apparatus 28

Figure 3.3 Canisters filled with wash solution and steel balls 29

Figure 3.4 Rinsing of fabric samples directly from tap water 30

Figure 3.5 Drying of samples on a line in clean fume hood 31

Figure 3.6 Extraction of volatiles from fabric samples in a vial immersed in oil-bath using SPME fibre.. 33

Figure 3.7 Kuderna-Danish evaporator prepared for concentration of directly extracted odorants from fabric samples... 35

Figure 3.8 Integration of peaks 37

Figure 3.9 Examples of normalizing peak areas of standards using dodecane. 38

Figure 3.10 Headspace analyses of frozen samples 41

Figure 4.1 Initial sorption and desorption of odorants by cotton and polyester after inoculation without washing. 43

Figure 4.2 Percentage (with error bars) of original odorants removed from textile fabrics after one inoculation/wash cycle 45

Figure 4.3 Effects of variables on the direct extraction (with dichloromethane) of odorants from cotton and polyester fabrics 47

Figure 4.4 Effects of variables on the headspace sampling of odorants from cotton and polyester at all wash levels 52

Figure A.1 Experimental daily plan.. 82

Figure C1 Calibration curve for direct extraction of octanoic acid from cotton and polyester... 86

Figure C2 Calibration curve for direct extraction of nonenal from cotton and polyester 87

List of abbreviations

2M3SB	2-methyl-3-sulphanylbutanol
3H3MH	3-hydroxy-3-methyl hexanoic acid
3M2H	(E)-3-methyl-2-hexenoic acid
3M3SH	3-methyl-3-sulfanylhexan-1-ol
3SH	3-sulphanylhexanol
3SP	3-sulphanylpentanol
4M3H	4-methyl-3-hexenoic acid
AE	Alcohol Ethoxylates
ANOVA	Analysis of Variance
CGSB	Canadian General Standards Board, 2001
df	degree of freedom
DSDMAC	distearyldimethylammonium chloride
DVB/CAR/PDMS	divinylbenzene/carboxoen/polydimethylsiloxane
F	F statistic
g	grams
GC-FID	Gas Chromatography- Flame Ionization Detector
g/m^2	grams per metre square
Gpg	grains per gallon
K-D	Kuderna – Danish
Hz	Hertz
ISO	International Standard Organisation
IVA	Isovaleric acid
L	Litre
LAS	Linear alkylbenzenesulfonate
Min	Minutes
mm	milimetre
mL	mililetre
N-C-R	Nonenal on Cotton and washed with Regular detergent
N-C-S	Nonenal on Cotton and washed with Sport detergent
N-P-R	Nonenal on Polyester and washed with Regular detergent

N-P-S	Nonenal on Polyester and washed with Sport detergent
OH	hydroxyl groups
O-C-R	Octanoic acid on Cotton and washed with Regular detergent
O-C-S	Octanoic acid on Cotton and washed with Sport detergent
O-P-R	Octanoic acid on Polyester and washed with Regular detergent
O-P-S	Octanoic acid on Polyester and washed with Sport detergent
P	P value
PTFE	Polytetrafluoroethylene
ppm	parts per million
R.H.	Relative Humidity
SPME	Solid Phase Micro-Extraction
SS	sum of squares
VOC	Volatile organic compounds
$\leq$	Less than or equal to
$>$	greater than
$\bar{x}$	mean
μL	microlitre
%	percentage
^{o}C	Degrees Celsius

Chapter 1

Introduction

1.1 Background

Body odour is considered a problem in most cultures worldwide. This is because body odour can be viewed as unsanitary and tends to be associated with poor hygiene practices (Munk, Johansen, Stahnke, & Adler-Nissen, 2001; Takeuchi, Yabuki, & Hasegawa, 2013). The axillary region (or underarm), in particular, is one of the most high-impact and distinctive odour sites on the human body (Takeuchi et al., 2013). Axillary odour is generated by the metabolism of apocrine sweat by gram-positive bacteria, predominantly aerobic corynebacteria, to produce odorous volatile organic compounds (VOCs) (Gower, Holland, Mallet, Rennie, & Watkins, 1994; Rennie, Gower, & Holland, 1991; Taylor, Daulby, Grimshaw, Jamesy, Mercerz & Vaziri, 2003). Control of VOCs through the use of deodorants, antiperspirants, and/or fragrances in order to mask and/or inhibit bacterial growth is a common practice. This practice has led to the development of a multi-billion-dollar industry with worldwide sales of deodorants alone reported to be US$18 billion per year (Everts, 2012).

Clothing worn next to the skin can sorb and retain a significant amount of axillary odour. Sorption can be due to the transfer of sweat and bacteria from the skin, as well as from odorous compounds, into the clothing where odour may be further generated and released from the fabric (Dravnieks, Krotoszynski, Lieb, & Jungermann, 1968). As a result, clothing can continue to smell even after removal from the body. Furthermore, the intensity and retention of the smell may differ depending on the fibre content of the clothing, as natural fibres (e.g., cotton and wool) were noted to be less odorous than synthetic fibres (e.g., polyester) (McQueen, Laing, Brooks, & Niven, 2007; McQueen et al., 2014; Munk, Johansen, Stahnke, & Adler-Nissen, 2001). Types of odorous compounds emitted from the human body can be numerous with aldehydes, alcohols, ketones, aliphatic/aromatic groups and carboxylic acids consistently being the most common and most odorous (Bernier, Kline, Schreck, Yost, & Barnard, 2002; Curran, Rabin, Prada, & Furton, 2005). The non-polar compounds (e.g., lipids) tend to adhere strongly to non-polar fibres (e.g., polyester) more so than to polar fibres (e.g., cotton), thus, increasing the retention of odour in polyester clothing (Munk et al., 2001; McQueen et al., 2014; 2008). This link between the sorption of compounds and the hygroscopicity of textile materials has been shown elsewhere (e.g., Saini, Okeme, Mark Parnis, McQueen, & Diamond, 2016).

A common method to eliminate body odour is by laundering clothing, however, it may not always be effective, as some residues of the odorants are retained in some textile materials even after washing (Munk et al., 2001). Furthermore, the residual odorants continue to accumulate as the clothing is worn and washed several times, consequently, shortening the life-span of clothing (McQueen et al., 2014). The type of detergents used in the laundry processes can be a factor in the incomplete removal of odorous compounds from clothing as detergents differ in the chemistry of their surfactant content (Munk et al., 2001; Smulders, Rähse, & Jakobi, 2007).

Anionic surfactants have a negative charge in water, thus, enabling easy removal and suspension of fats and oils during laundering. However, high water hardness (Mg/Ca grains per gallon (gpg)) reduces the efficiency of anionic surfactants. Non-ionic surfactants, on the other hand, are not affected by water hardness as they do not have any charges in water (Obendorf & Webb, 1987; Smulders et al., 2011). As water hardness in Canada ranges from 1 to 62.5 gpg Mg/Ca, the hardness may have some effect on the efficiency of laundering, even though water is softened for domestic use (Water hardness in Canada, 2016). In view of this, recent detergents are produced with both anionic and non-ionic surfactants (Ceresana Market Institute, 2015).

Thus textile materials, odorous compounds and laundry detergents appear to have a major influence on the effective removal of body odour from clothing after being worn multiple times. Yet, to date, little research has been conducted that examined the interplay of the chemical properties of these factors in the problem of body odour.

1.2 Statement of problem and purpose

1.2.1 Statement of problem

Body odour is formed when sweat from the axillary region is metabolised by bacteria. This results in odorous compounds that can then be transferred to the clothing worn in close proximity to the skin. The odorous compounds, and the textile fibres that make up the clothing, differ in their chemistry, resulting in some compounds strongly adhering to textile materials. Laundering is meant to eliminate odour but is not always effective as it is influenced by the polarity of the textile material and odorous compounds, and the effectiveness of the detergents in the laundry process. As a result, there may be an incomplete removal of some of these compounds which then accumulate after several usages and wash cycles. Consequently, more energy, chemicals and water are used in laundry. Even with that, after multiple usages the clothing may become odorous and undesirable to the wearer. This may result in clothing being discarded before the end of their expected lifespan.

1.2.2 Purpose

The purpose of this study was to investigate the retention of selected odorous compounds on selected textile materials, after being exposed to odorants, and washed up to 10 times, using two selected commercial detergents. The focus of the study was on the odorous compounds and not the bacteria or sweat. The intention was to gain an in-depth understanding of the relationship that exists between odorants and textile materials, in conjunction with the effect of different laundry detergents. Understanding this relationship could be essential in creating more effective laundry detergents and deodorants that can target specific odorants for the type of textile material.

1.3 Objectives

The objectives of the study were:

a) To determine the quantities of odorous compounds retained within and released by polyester and cotton textile fabrics before and after multiple inoculation/wash cycles.

b) To determine the efficiency of two selected detergents in the removal of odorous compounds from polyester and cotton.

Chapter 2

Review of Literature

2.1 Development of body odour

2.1.1 Sweat and sebum

Sebaceous glands and sweat glands (i.e., eccrine, apocrine and appoecrine) are present in human skin secreting moisture, salts and oily substances at the skin surface. Oil and nutrients are provided by sebaceous glands at the skin surface and are evenly distributed over most areas of the body (Leidal, Rapini, Sato, Ung, & Sato, 1982). They discharge accumulated lipid droplets which eventually fragment to form sebum. Sebum contains: lipids, including acyclic triterpene and squalene (C_{30}) in high concentration; cholesterol; and free fatty acids (methyl-branched) (Montagna & Prakkal, 1974; Greene, Downing, Pochi, & Strauss, 1970).

Eccrine sweat glands provide moisture that helps to thermo-regulate the body by enhancing heat loss through evaporative cooling. The secretions are odourless and consist of water, with small traces of salts (sodium chloride), proteins, amino acids, urea, ammonia and lactic acid (Smallegange, Verhulst, & Takken, 2011). In the axillary region, eccrine glands are equal in number to apocrine glands; however, apocrine glands are found deep in the dermis (Leidal et al., 1982).

Apocrine glands release excretions as a response to stress and sexual stimulation (Leidal et al., 1982). The secretion is a milky, grey or reddish fluid with a gluey consistency that contains odourless fats in the form of fatty acids like valeric (C_5), caproic (C_7) and caprylic (C_8) acids. Other constituents include proteins, lipids and non-odiferous steroids (Hamada et al., 2014; Smallegange et al., 2011). Specifically, in the foot and axillary regions, either staphylococcal or aerobic coryneform species dominate the microflora most individuals carry (Kanda et al., 1990; Taylor et al., 2003). A strong correlation was found between a high population of corynebacteria and strong axillary odour formation (Taylor et al., 2003). However not all corynebacteria produce odour as 30% of the subjects examined by Rennie et al., (1991) did not carry odour-producing corynebacteria or the bacteria were in low numbers (Rennie et al., 1991). In the feet, however, high densities of exoenzyme-producing microorganisms were strongly linked to intense odour (Marshall et al., 1988). Likewise, *Bacillus subtilis* have been linked with strong foot odour as a significant amount of the bacteria were found in the plantar skin of subjects with strong foot odour (Ara et al., 2006). On the other hand, *Staphylococcus capitis* and Malassezia fungi are responsible for odour formation in the hair when they metabolise sebum from the scalp (Yamamoto, Shimosato & Okada, 1998).

2.1.3 Odorous compounds

The mechanism of odour formation starts when odour-causing bacteria metabolise nourishments available in sweat. This leads to the formation of odorous VOCs (Gower et al., 1994; Rennie, Gower, Holland, Mallet, & Watkins, 1990). For instance, staphylococci metabolise lycerol and lactic acid found in apocrine sweat leading to the generation of short-chain (C_4-C_5) methyl acids. The actions of staphylococci may also produce acetic and propionic acids which contribute to the axillary odour profile (James, Hyliands, & Johnston, 2004; Moat et al., 1988). Troccaz et al., (2004) also isolated a variety of bacterial species and found the *Staphylococcus haemolyticus* strain to produce the most sulphur in sweat. The strain was incubated with sterile sweat and produced compounds including 3-methyl-3-sulfanylhexan-1-ol, which sniffers identified to have a sweaty and onion-like smell (Troccaz, Starkenmann, Niclass, van de Waal, & Clark, 2004).

In addition, corynebacteria convert fats and Cys-Gly-(S) in sebum and apocrine lipids to produce triglycerides leading to the formation of 3-methyl-3-sulfanylhexan-1-ol (3M3SH) (Emter & Natsch, 2008; James et al., 2004). Propionibacterium species, on the other hand, are responsible for the fermentation of glycerol from hydrolysed triglyceride and lactic acid to generate acetic acid (C_2) and propionic acid (C_3) (Moat & Foster, 1988).

Furthermore, amino acids in sweat can also be processed by propionibacteria and staphylococci to produce odorous short-chain (C_4-C_5) methyl-branched fatty acids such as isovaleric acid (IVA) (Thierry, Maillard, & Yvon, 2002). IVA is one of the many short-chained fatty acids known to be associated with an acidic note of axillary odour (Labows et al., 1982) as well as foot odour (James, Cox, & Worrall, 2013). The Moraxella species were also recently found to be responsible for malodour in laundry as they produce 4-methyl-3-hexenoic acid (4M3H) identified as "acidic or sweaty odour" or "wet-and-dirty-dustcloth-like malodour" (Kubota et al., 2012).

Odorous compounds have been found all over the human body (Ara et al., 2006). In the hair, scalp sebum is degenerated by the microflora with "strong lipase activities" to form short-chain fatty acids and aldehydes that are among the primary contributors to hair odour profile (Yamamoto et al. 1998). Similarly, isomers of short-chain fatty acids, especially IVA make up foot odour (Kanda et al., 1990). IVA can be formed when kytococcus decomposes foot callus into leucine (James, Cox, & Worrall, 2013) and/or when staphylococcus epidermis metabolises leucine (Ara et al., 2006). In the axillae, however, the odorous compounds are highly diverse with fatty acids (Zeng et al., 1991), 16-androstene steroids (Natsch, Schmid, & Flachsmann, 2004), sulfanylalkanols (Troccaz et al., 2004) considered significant contributors to axillary odour profile (Kanlayavattanakul & Lourith, 2011).

Carboxylic acids make up a significant component of the characteristic axillary odour with the major contributor being (E)-3-methyl-2-hexenoic acid (3M2H) (Zeng et al., 1991). However, more recently, 3-hydroxy-3-methyl hexanoic acid (3H3MH) has been identified as the most pungent and abundant odorant in axillary secretions (Hasegawa, Yabuki, & Matsukane, 2004; Natsch et al., 2004). In another study, textile materials were soiled with sebum and washed; the washed solution was then matched against the unwashed samples. Results showed 4-ethyl octanoic acid to be the most powerful acidic odorant in both washed and unwashed extracts (Munk, Münch, Stahnke, Adler-Nissen, & Schieberle, 2000).

Also known as caprylic acid, octanoic acid was found when the human scent was collected with cotton, viscose rayon, wool and polyester in a recent forensic investigation (Prada, Curran, & Furton, 2011).

Sulphanylalkanol compounds including 3-sulphanylhexanol (3SH), 2-methyl-3-sulphanylbutanol (2M3SB), 3-sulphanylpentanol (3SP), and 3-methyl-3-sulfanyl-hexanol (3M3SH) were found in apocrine secretions from the axillae in low quantities (Natsch et al., 2004). Other contributors to axillary odour include sulphurous compounds (thiols) which are known for their repulsive and onion-like odour (Andersen & Bernstein, 1975). When *Corynebacterium* C-S lyase metabolises these compounds very pungent thiols are released (Natsch et al., 2005; Starkenmann, Niclass, Troccaz, & Clark, 2005; Troccaz, Benattia, Borchard, & Clark, 2008). Despite their low concentration, thiols strongly contribute to the typical body odour profile (Hasegawa et al., 2004), and human sensitivity to them is high (Kanlayavattanakul & Lourith, 2011). But due to their extremely low concentrations, they are very difficult to detect instrumentally and therefore have not been detected in the instrumental head-space analysis of odour released from fabrics.

Also present in axillary odour are steroids (Decréau, Marson, Smith, & Behan, 2003; Gower, Mallet, Watkins, Wallace, & Calame, 1997). The 5, 16-androsteadien-3-Beta-ol (androstadienol) and 4, 16-androstadien-3-one (androstadienone) contents of apocrine sweat are converted by corynebacteria into steroids resulting in urine and musk-like smells. The steroids are a mixture of 5α-androstenone, 5α-androst-16-en-3α-ol and 5α-androst-16-en-3α (3α and 3β -androstenols) (Gower, Holland, Mallet, Rennie, & Watkins, 1994; Rennie, Gower, Holland, Mallet, & Watkins, 1990).

Other volatiles emitted from the axillary region include ketones, aliphatic, aromatic compounds and very notably, aldehydes (Gozu et al., 2000; Munk, et al., 2001; Munk et al., 2000; Zeng et al., 1991). A major aldehyde identified in axillary odour is 2-nonenal which is formed when hexadecanoic acid in sebum is decomposed by bacteria (Gozu et al., 2000). Haze et al., (2001) was the first to report 2-nonenal as human odour associated with old-age. An unsaturated aldehyde, 2-nonenal has an unpleasant greasy and grassy odour with the threshold value for detection of about 3-4 parts per million (ppm) in paraffin oil solution (Stahl, 1973). Furthermore, 2-nonenal was shown to have strong adhesion to polyester due to its hydrophobicity (Munk et al., 2001), and has been used as a compound representing body odour in the recent international standard test method for measuring the deodorancy of textile fabrics (International Standards Organization, 2014).

2.2 Textile fibres and fabrics

Clothing serves several purposes including protection and aesthetics; however, comfort remains the most important factor in purchasing clothing (Bartels, 2005; Liu & Little, 2009). Optimum comfort in clothing is achieved by exploiting the chemical and physical properties of both synthetic and natural textile materials. Specifically, the ability of textile fibres to sorb perspiration in both vapour and liquid form and then pass it on to the surrounding air enhances the level of sensorial comfort they provide (Brotherhood, 2008). For this reason, the high absorbency of cotton and the versatility of polyester have been relied on for a long time to provide the optimum comfort in clothing (Havenith et al., 2013; Liu & Little, 2009; Okubo, Saeki, & Yamamoto, 2008; Prahsarn, 2005; Yoon & Buckley, 1984).

2.2.1 Cotton and polyester fibres

2.2.1.1 Cotton

Globally cotton is the most important natural fibre. Despite dropping from 68% of worldwide consumed fibres in 1960 to 40% (2006) and now 25% (2015), due to the advent of new synthetic fibres, it continues to be the most preferred natural fibre (Chaudhry, 2010; Hämmerle, 2011; Wakelyn et al., 2006). Moreover, in the US alone cotton consumption is expected to rise to 26 million metric tons by 2025 (Hämmerle, 2011).

Cotton is a natural fibre composed of 95% cellulose at the raw state (Guthrie, 1955) and 99%

after treatments that remove the non-cellulosic components of the fibre (McCall & Jurgens, 1951). The cellulose polymers are long, linear chains of glucose that are connected by hydrogen bonds as illustrated in Figure 2.1 (Wakelyn et al, 2006). In the glucose units of cellulose, there are a large number of hydroxyl groups (-OH) that make cotton hygroscopic and have a regain of 7-8.5% at 20 °C and 65% relative humidity (Canadian General Standards Board, 2001). This allows the fibre to attract water into its structure resulting in high absorbency and affiliation to polar substances (Kadolph, 2010). When worn next to the skin, it allows moisture to freely pass through for evaporation and cooling, leaving the wearer feeling comfortable (Wakelyn et al., 2006).

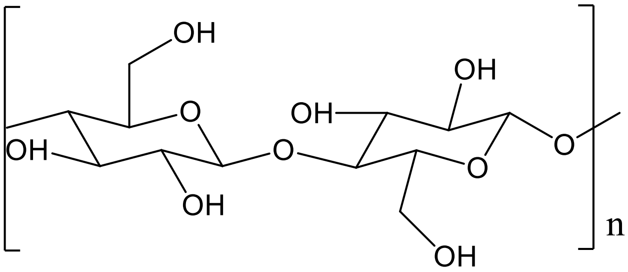


Figure 2.1 Chemical structure of the cotton fibre (Designed using ChemDraw®)

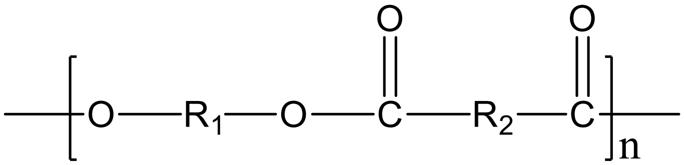
Furthermore, the dynamic surface wetness of fibres has been shown to be an integral factor in moisture management as it determines how well a fibre collects and passes moisture to the environment for drying (Das & Alagirusamy, 2010). It was suggested that there exists a mobile water film on the internal surface of the cotton fibre due to the presence of numerous micropores on the cotton cellulose polymer. This allows free "side-to-side" mobility of water in cotton compared to polyester, where the micropores are absent (Scheurell, Spivak, & Hollies, 1985).

However, recent studies have shown that despite cotton's high affinity and moisture regain, its dynamic surface wetness is poor. This is because when cotton sorbs moisture, it swells and reduces the size of air spaces causing a delay in wicking or moisture transfer (Das, Kothari, Fangueiro, & Araújo, 2007; Pause, 1996). Although cotton has typically been perceived to have lower odour intensity than polyester fabrics (McQueen et al., 2007) cotton can still emit odour and cotton products have been widely used in collecting human odour for textile science (Munk et al., 2001; McQueen et al., 2014) and forensics (Curran, Prada, & Furton, 2010; Sommerville, Mccormick, & Broom, 1994).

2.2.1.2 Polyester

Polyester is the most used synthetic fibre with a global production capacity in an excess of 4 million metric tonnes (Smith & Mei, 2013). Currently, it accounts for 50% of all produced fibres worldwide (Fibre2fashion, 2017). It is also the fibre most frequently blended with cotton in the production of apparel of all kinds (Kothari, 2008). In 2016, apparel production covered 50% of polyester total end uses while home furnishing was second with only 25% (Fibre2fashion, 2017).

Polyester fibre is a manufactured fibre “composed of linear macromolecules having, in the chain, at least 85% by mass of an ester of a diol and terephthalic acid” (Agrawal & Jassal, 2008). The most common form of polyester fibre is polyethylene terephthalate (PET), produced by a reaction of terephthalic acid or dimethyleterephthalate with ethylene glycol (East, 2005). Polyethylene terephthalate is characterized by having a benzene ring in the main chain as shown in Figure 2.2. The benzene ring is necessary to give firmness to the structure and although the Van der Waal’s interactions are not as strong as hydrogen bonds, the close packing of the benzene ring enables crystallization. Polyester is nonpolar with no available groups for making hydrogen bonds.



$$\left[O-R_1-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2-\overset{\overset{\displaystyle O}{\|}}{C} \right]_n$$

Figure 2.2 Chemical structure of polyester fibre, $R_1 = CH_2\text{-}CH_2$; R_2 = Benzene ring (Designed using ChemDraw®)

Therefore, polyester fabrics are characterized by low moisture regain (0.4-0.6% in 65% Relative Humidity (R.H)) with problems such as the build-up of electrical charges and retention and redeposition of soils (especially oily soils). Difficulties associated with laundering also occur (East, 2005; Kadolph, 2010).

Polyester also has a problem with a bacterial odour which is a result of a build-up of soil on the fabric, promoting bacterial growth (Callewaert et al., 2014). Low moisture regain and its light weight also means polyester dries quickly compared to cotton. Cotton tends to absorb and retain moisture and therefore takes considerable time to dry (Kadolph, 2010). However, moisture does not escape from between the skin and polyester fabric except through capillary action (wicking) (Buckley, 2016; Kissa, 1996; Manshahia & Das, 2014). Despite the wicking ability, the poor wettability of polyester may result in it feeling uncomfortable to wear next to the skin (Kadolph, 2010).

2.2.2 Interaction of textiles with body odour

As explained above, a fibre's moisture management starts with an effective wetting and wicking process (Kissa, 1996; Patnaik, Rengasamy, Kothari, & Ghosh, 2006). Wetting ability of fibres was examined in an interaction between liquid sweat/fibre/malodour by inoculating isovaleric acid onto untreated wool, cotton and polyester materials. Using liquid scintillation counting after 3 hours and 20 hours of exposure, 98% of isovaleric acid was recovered from wool, 50% from cotton and polyester released all of the isovaleric acid. This can be attributed to the swelling differences between these fibres as cotton swells and can accommodate more liquid than both polyester and wool (Hammer, Berner-Dannenmann, & Hoefer, 2013).

Swelling is the change in fibre structure that results from a physio-chemical interaction with liquid sweat containing odorous compounds (Cantergiani & Benczédi, 2002; Liu, Obendorf, Leonard, Young, & Incorvia, 2005). Another study examining aroma compounds showed various aromas distributed throughout the diameter of the cotton fibre in contrast to the patchy distribution on polyester fibre surface (Liu et al., 2002). Fragrances also bonded well with the amorphous and microcrystalline parts of cotton towels at relatively higher humidity environments (Cantergiani & Benczédi, 2002).

The adsorption of either sweat or odorants can vary due to the differences in polarity of both the odorants and the textile materials. Cotton is polar and was shown to easily sorb dipole compounds in high quantities while polyester yarn adsorbed lesser amounts of dipole compounds due to its lower polarity (Yao, Laing, Bremer, Silcock, & Leus, 2015). Recent studies showed polyester to strongly bond with hydrophobic odorants including (Z)-4-heptenal, (E)-2-nonenal, and guaiacol more so than with 3-methylbutanoic acid and 4-methyloctanoic acid. In contrast, cotton retained less of all odorants (Munk et al., 2001). The odorants on polyester had similar intensity, with or without wash, after a day, while the intensity odorants on cotton reduced drastically. It was attributed to the hydrophobic nature of polyester, which causes lipid (hydrophobic) compounds to adhere strongly to the fibre and makes removal challenging (Munk et al., 2001).

In another study, McQueen et al., (2008) found a negative correlation between moisture regain and odour intensity for wool, cotton and polyester fabrics: as the moisture regain of the fabric increased, the perceived odour intensity decreased. This could indicate that there may be a relationship between the fibre's ability to absorb moisture vapour and odorous volatile compounds from the environment.

2.2.3 Interaction between sweat and bacteria in textile materials

In addition to differences in moisture management, there exists a difference in microbial growth, depending on the fibre content of clothing leading to a possible generation of odour (Callewaert et al., 2014; Teufel et al., 2010). The investigation into the colonization of bacteria on textile revealed that synthetic fibre materials (polyamide and polyester) showed the highest bacterial mass compared to the cellulosic based materials (cotton and lyocell) (Teufel et al., 2010). The high bacterial mass present on polyester suggests that there are more bacterial interactions on polyester than on cotton causing the increased formation of odour. This can be due to the extra warmth and the moist environment created in the axillary when synthetic clothing is worn (McQueen, Laing, Delahunty, Brooks, & Niven, 2008).

In another study, 26 subjects exercised while wearing cotton and polyester t-shirts before the t-shirts were incubated for 28 hours and later analysed. Results showed micrococci on almost all synthetic t-shirts while staphylococci were found on both polyester and cotton fabrics. The presence of these bacteria was linked to the more offensive smell polyester had over cotton (Callewaert et al., 2014)**.** On the other hand, the hydrophilic nature and porosity of cotton caused the generation of higher odour during storage in wet conditions than it did on polyester. This can be due to the nourishment available in natural fibres and the damp condition provides a favourable environment for the growth of microorganisms (Munk et al., 2001). However, various studies have concluded that cotton smells less than polyester after washing (Munk et al., 2001; Chung & Seok, 2012; McQueen et al., 2014). This could be due to the ease with which microbes are released from cotton after washing, as the higher microbial count was found in the wash liquor of cotton when compared to polyester (Munk et al., 2001).

Despite bacteria being the main cause of axillary odour, to begin with, there is still evidence that bacterial species survive better on fabrics made of natural fibres compared with synthetic fibres such as polyester (McQueen, Laing, Brooks, et al., 2007). So the physio-chemical properties of the textile fibres and the odorants or precursors to odour (e.g., sebum, apocrine sweat) may be more influential than bacteria in the intensity of the odour following wear against the skin.

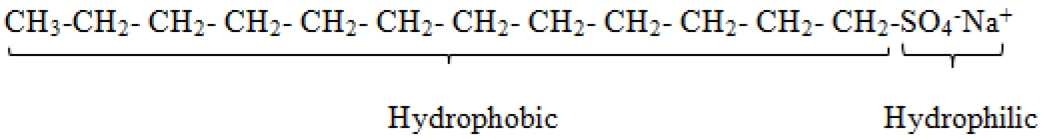
2.3 Laundering to remove odours from clothing

Laundering is the most common way of eliminating odours and dirt from clothing; however, it may not always be effective in the complete removal of odour. This may be due to the various chemical interactions between the key factors in laundering and the different interactions between odours and textile materials as discussed earlier (McQueen et al., 2014; Munk, Johansen, Stahnke, & Adler-Nissen, 2001). The key players in the laundry process include detergents, water, temperature, agitation and the duration of washing. Detergency, however, is the most important factor and has resulted in a $60 billion market that continues to grow in strides (Scheibel, 2004).

2.3.1 Detergency

A household detergent is a complex formulation cleaning agent containing surfactants that “do not precipitate in hard water and have the ability to emulsify oil and suspend dirt” (Celanese Acetate, 2001). Until the 20th century, the only choice of detergent was soap. It was obtained by the formation of a sodium or potassium salt and a fatty acid or mixture of fatty acids (Schiebel 2004). Since World War I, synthetic detergents have replaced soap in many household applications (Linke, 2009).

Ingredients in detergents serve specific purposes in the washing process. They include surfactants (for dissolving oily soils), oxidants (for bleaching), builders (for reducing water sensitivity) and others for inhibiting the growth of bacteria or fungi (Linke, 2009). However, surfactants are the most important group of ingredients in all types of detergents comprising from 15 to 40% of the total detergent formulation (Smulders & Sung, 2012; Scheibel 2004). Surfactants are water-soluble surface-active agents comprising of a hydrophilic portion attached to hydrophobic or solubility-enhancing functional groups as illustrated in Figure 2.3 (Scheibel, 2004).



$$\underbrace{CH_3\text{-}CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2\text{-}\ CH_2}_{\text{Hydrophobic}}\text{-}\underbrace{SO_4^-Na^+}_{\text{Hydrophilic}}$$

Figure 2.3 Structure of a surfactant

Surfactants act by modifying the surfaces by lowering the surface tension of a liquid, and the interfacial tension between two liquids (Linke, 2009). In addition, not only do they loosen and remove soil, surfactants also emulsify, solubilize or suspend soils in the wash solution (Bajpai & Tyagi, 2007). Moreover, surfactants also display differences in how effective they are in removing odour due to variations in water hardness, chemistries of textile materials and odorous compounds or soils that act as precursors to odour (Bajpai & Tyagi, 2007; Smulders & Sung, 2012). There are four categories of surfactants largely based on their reaction to water hardness, fabric types and soils: cationic, amphoteric, anionic and nonionic surfactants.

2.3.1.1 Cationic surfactants

Cationic surfactants are compounds with a positively charged nitrogen atom and at least one hydrophobic, long chain of the alkyl group substituent in the molecule. This allows the surfactant to dissociate in water into a non-amphiphilic cation and an anion (Salaguer, 2002). Cationic surfactants are often used as bactericides and/or to adsorb on negatively charged substrates to produce anti-static and hydrophobic effects (Salaguer, 2002). An example of a cationic surfactant is distearyldimethylammonium chloride (DSDMAC) which is a long-chain surfactant with particularly high sorption power to many surfaces, especially to natural fibres like cotton but less on synthetics (Smulders & Sung, 2012).

2.3.1.2 Amphoteric surfactants

Amphoteric surfactants contain both cationic and anionic groups even in an aqueous solution which makes it amphiphilic (double affinity). This allows amphoteric surfactants to have an affinity for both polar and non-polar substances. Its polar content may be composed of an alcohol, thiol, ester or acid, therefore, having an affinity for water, while the non-polar part may be composed of a hydrocarbon chain of the alkyl or alkylbenzene type (Smulders & Sung, 2012; Salaguer, 2002). Alkylbetaine or alkylsulfobetaine is a common type of amphoteric surfactant, however, it is used mostly in manual dishwashing and not in laundry (Smulders & Sung, 2012).

2.3.1.3 Anionic surfactants

In anionic surfactants, carboxylates, sulphates, and phosphates usually make up the hydrophilic part of the surfactant while a 12-16 carbon atom hydrophobic chain is preferred for optimum detergency (Bajpai & Tyagi, 2007; Scheibel, 2004). Anionic surfactants dissociate in water into an amphiphilic anion that allows them to easily remove grease and oil and outperform all other detergents including bleach and enzymes (Salaguer, 2002; Scheibel, 2004). The use of anionic surfactants such as soap has declined due to their sensitivity to water hardness that leads to the formation of lime soap. Lime soap accumulates on fabrics and acts to reduce the absorbency, air permeability and eventually can develop malodours. On the other hand, linear alkylbenzenesulfonate (LAS), an anionic surfactant, has better detergency performance than soap as it has superior foaming characteristics which can easily be stabilized by foam stabilizers. Anionic surfactants are therefore often included in liquid detergents despite some sensitivity to water hardness (Salaguer, 2002; Smulders & Sung, 2012).

2.3.1.4 Nonionic surfactants

Nonionic surfactants have a hydrophilic group such as alcohol, phenol, ether, ester, or amide that is of a non-dissociable type. Thus nonionic surfactants do not ionize in solution (Bajpai & Tyagi, 2007; Salaguer, 2002). Water hardness sensitivity is also avoided as there are no charges which can be deactivated by hard water. Therefore, non-ionic surfactants tend to be very efficient at removing oily soils through solubilisation and emulsification of the soils (Bajpai & Tyagi, 2007; Salaguer, 2002). A common example of the nonionic surfactant is the alcohol ethoxylate (AE). It has no electrostatic intersections and can be adjusted to have a hydrophilic-lipophilic balance value in water. However, the presence of polyvalent cations reduces the negativity in electro-kinetics in colloidal dispersions (zeta potential) found on fibre surfaces and soil, leading to reduced repulsion and poor soil removal (Smulders & Sung, 2012).

To counter some of these problems and maximize the performance of surfactants, two or more surfactants may be mixed together in some powder or any liquid detergents to improve efficiency and reduce contamination of the environment (Bajpai & Tyagi, 2007; Zhu & Feng, 2003). A mixture of both nonionic and anionic surfactants results in more stabilized polymer particles and consequently more efficient detergents. An equal amount of anionic and cationic surfactants is not effective as they neutralize to form a salt that acts like additional greasy soil. However, a little amount of specific cationic surfactant to anionic or nonionic surfactant can greatly enhance detergency performance (Smulders, Rähse, et al., 2007). For these benefits and others, there are many detergents on the market that mix different surfactants together. For example, both Tide® Free and Gentle and Tide® Plus Febreze Freshness Sport liquid detergents, have both anionic (benzenesulfonate) and nonionic (alcohol ethoxylates) surfactants together as part of their key ingredients (Household Products Database, 2017).

2.3.2 Water hardness and temperature

Water serves primarily as the solvent for detergent and for soluble salts within the soil. Not only does water serve as a medium of dispersion of soil but it also wets and penetrates fabrics for effective adsorption of detergent (Smulders, Rybinski, et al., 2007). For optimum water efficiency, detergents are required to reduce the surface tension of water from 72 mN/m to 30 mN/m. However, ion exchange between the surfactant and water can also form insoluble calcium and magnesium ions which can hinder the removal of soil and even form residues on fabric (Smulders, Rybinski, et al., 2007). Builders in detergents nonetheless are able to form non-reversible reactions with these ions, especially with calcium to soften water, and also help to prevent redeposition of soil (Leidreiter, Gruning, & Kaseborn, 1997).

The temperature of the water also influences the efficiency of detergents and the laundry process at large. Increasing the temperature of the water was found to increase water power in washing (Smulders, Rybinski, et al., 2007). Earlier researchers have examined the effect of water temperature in the removal of pesticides from clothing. Generally warm (49 °C) or hot (60 °C) water has been more effective in removing pesticides from typical work wear clothing such as denim than cold water (30 or 40 °C) (Easley, Laughlin, Gold, & Schmidt, 1982; Kim, Stone, &

Sizer, 1982). However, a global campaign for sustainability encourages the use of cold water in the laundry which unfortunately limits the efficiency of LAS as it forms multilayered vesicles with high water hardness and low temperature (Scheibel, 2004). In contrast, AE surfactant has long been found to be more efficient in hard water than LAS although the temperature of the water examined was higher (52 ^{o}C) (Illman, Albin, & Stupel, 1972). Therefore, using the right temperature for laundering is crucial to its efficiency.

2.3.3 Soiling and build-up of odour

2.3.3.1 Soiling

Soiling is when textile materials are stained or smudged, during use or in storage, from undesirable substances such as oil, dirt and dyes (Celanese Acetate, 2001). Clothing can be soiled from the environment or from human sources, although typically mixtures from both are observed. Laundering is the most commonly employed method for removing soils (Venkatesh, Dweltz, Madan, & Alurkar, 1974). For the laundering process to be efficient, the chemical properties of the soil on fabric are very important (Bowers & Chantery, 1969; Obendorf & Webb, 1987). Studies have shown that there is considerable variability in the type of soil present on clothing; water-soluble and insoluble particles, output of sebaceous glands, lipids as well as particles from the immediate environment (e.g., cosmetics, dust and smoke) have all been detected (Lloyd & Adams, 1989; Smulders et al., 2011).

Other types of soiling include odorants, especially those from the axillary region of the human body (McQueen, Laing, Brooks, et al., 2007). In most cases, a mixture of soils mentioned above is collected into clothing which makes the work of surfactants and other ingredients in detergents even more crucial (Smulders et al., 2011). Sebum, for instance, is a natural collection of lipids secreted by the sebaceous glands. It contains a mixture of triglycerides, fatty acids, mono and di-glycerides and other compounds. Sebum can migrate into fabrics and bind other soils such as clay and metal oxides to fabric very strongly (Lloyd & Adams, 1989; Bowers & Chantrey, 1969). Additionally, due to the variation in size, geometry and chemistry, each soil type is treated specially and some need to be chemically broken down before they can be removed (Bowers & Chantery, 1969; Obendorf & Webb, 1987).

Sorption of odorants, water and surfactants by fabrics was found to be highly dependent on the fibre surface area, pore structure and chemical structure of the fibre (Liu et al., 2005; Munk et al., 2001; McQueen et al., 2014; Obendorf & Webb, 1987). A significant difference in sorption of aroma and detergents was apparent between untreated and mercerized cotton fabrics which were attributed to the variation in fibre morphology (Liu et al., 2005).

While fibre morphology was not found to influence the location of soils on natural fibres, SEM showed the influence of fibre morphology in the distribution of oily soil on synthetic fibres. There was oily soil found across the surface of polyester and cotton fibres, between fibre spaces in the yarns, as well as in the crenulation, secondary walls, and lumen of cotton fibres (Bowers & Chantrey, 1969). Moreover, aging of soil on the surface of, or in, fibres can increase the tenacity of stains and darkens soils causing some difficulty in the laundry. Furthermore, the chemistry of laundry elements can accelerate aging of soil in fabrics and form deposits that are difficult to remove (Lloyd & Adams, 1989). Soils which are odorous may be 'invisible' but a similar process could be occurring with ageing and difficulty of removing odorous soils over time.

2.3.3.3 Odour build-up

Odour in clothing has been shown to accumulate over several wears and wash cycles largely due 2001). Although odour intensity on both cotton and polyester was significantly reduced following laundering, the laundering process was more effective in removing odour from cotton than from polyester. This disparity can be attributed in part to the interplay between the chemistries of the soiled fibres and odorants (Smulders & Sung, 2012; Scheibel, 2004).

While C4-C8 chained carboxylic acids were released in the headspace above both cotton and polyester fabrics following wear, but prior to laundering, lower total peaks were found for cotton than for polyester after washing (McQueen et al., 2014; Munk et al., 2001). Similarly, despite similar absorption by cotton and polyester, sebum was more difficult to remove from polyester (hydrophobic) due to its poor dynamic surface wetness (Bowers & Chantrey, 1969; Das & Alagirusamy, 2010).

Therefore, the chemical type of the soil and the bond it forms with the substrate are more important than the amount of soil absorbed (Bowers & Chantrey, 1969). As a result, the hydrophilicity of cotton allows more semi-polar acids to be easily absorbed by the polar cotton polymer (Yao et al., 2015). On the other hand, polyester has a complex odour profile with aldehydes such as 2-nonenal as the dominant compounds emitted that can be difficult to remove during laundering (Munk et al., 2001). However, cotton is negatively charged in water and has a large amount of calcium on its surface which increases water hardness and causes the removal of soil to be challenging (Smulders, Rybinski, et al., 2007).

Consequently, results from both sensory assessments and chemical analysis expounded the inefficiency of laundry in the removal of odorants from textile materials regardless of fibre types (McQueen et al., 2014; Munk et al., 2001). The residual acids and other odorants from every wear/wash cycle continued to accumulate on cotton and polyester over 20 wear/wash cycles as reported by McQueen et al., (2014). In addition, unlike wool and cotton, odour continued to develop on polyester even when it was not in contact with the human axillary region (McQueen et al., 2008). It was also suggested that odour is formed when clothes are re-worn, rewetted, and heated to body temperature, as surviving odour-forming bacteria continue to build-up over time (Munk et al., 2001). Again, aging increases the tenacity of stains and darkens soil causing some difficulty in laundering. Moreover, through repeated washing, soil and odorants can change from a simple coating on fabrics to the final ageing and soiling level; colloidal deposits or molecular absorbates (Lloyd & Adams, 1989). This eventually causes clothing to lose its sensorial comfortability during wear.

Chapter 3

Methods

3.1 Experimental design

The experimental design was a 2 x 2 x 2 x 3 factorial design. Two odorants (4-ethyl-octanoic acid, 2-nonenal), two fibre types (cotton, polyester), two detergents (regular, sport) and 3 inoculation/wash levels (1, 5, 10) were the independent variables under investigation. The peak areas of 4-ethyl octanoic acid (octanoic acid) and peak areas of 2-nonenal (nonenal) for headspace and direct extraction were the dependent variables. The design is shown in Table 3.1. Appendix A (Figure A1) also shows details of the daily plan for the execution of the experiment over 30 days.

3.2 Materials and chemicals

3.2.1 Experimental fabrics

Test fabrics were supplied by Cotton Incorporated (North Carolina, USA). Fabrics used in the study were 100% cotton and 100% polyester interlock knit fabric structures with similar weight and thickness (Table 3.2). Upon fabric acquisition, the fabrics were laundered five times with Tide® Free & Gentle detergent, (Proctor & Gamble) and then machine dried. This was done to stabilize the fabric structure and remove possible finishes that could have influenced test results.

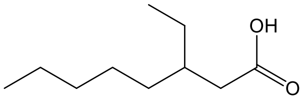
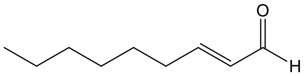
3.2.1.1 Measurement of fabric physical properties

Each fabric sample was conditioned before testing all physical properties (i.e., fabric mass and thickness) according to CAN/CGSB-4.2 No.2-M88 (Canadian General Standards Board, 2001) at a temperature of 20°C ± 2°C and a relative humidity of 65% ± 2% for at least 24 hours. All specimens were cut with 50 mm diameter from the conditioned fabric. Standard test methods were used to characterize the fabric properties, such as mass per unit area and thickness. Tests of a unit mass of fabrics were taken under CAN/CGSB-4.2 No.5.1-M90 (Canadian General Standards Board, 2013), and thickness under CAN/CGSB 4.2 NO.37-M 87 (CGSB, 2002).

Table 3.1 A 2 x 2 x 2 x 3 factorial design: 2 odorous compounds x 2 fabrics x 2 detergents x 3 wash levels

			Odorous compounds	
Fabric	Detergent	Wash level	Octanoic acid (O)	Nonenal (N)
Cotton (C)	Regular (R)	1	O-C-R-1	N-C-R-1
		5	O-C-R-5	N-C-R-5
		10	O-C-R-10	N-C-R-10
	Sport (S)	1	O-C-S-1	N-C-S-1
		5	O-C-S-5	N-C-S-5
		10	O-C-S-10	N-C-S-10
Polyester (P)	Regular (R)	1	O-P-R-1	N-P-R-1
		5	O-P-R-5	N-P-R-5
		10	O-P-R-10	N-P-R-10
	Sport (S)	1	O-P-S-1	N-P-S-1
		5	O-P-S-5	N-P-S-5
		10	O-P-S-10	N-P-S-10

Table 3.2 Experimental materials

a. Fabrics		
Name	100% Cotton	100% Polyester
Mass	234 g/m^2	224 g/m^2
Thickness	1.28 mm	1.31 mm
Fabric structure	Interlock knit	Interlock knit
Wales	18 stiches/cm	16 stiches/cm
Courses	14 stiches/cm	14 stiches/cm
b. Odorous compounds		
Name	4-ethyl octanoic acid	2-nonenal
Chemical structure		

Chemical structures were designed using ChemDraw®

3.2.2 Chemical compounds

Odorous compounds used in the study were 4-ethyloctanoic acid (octanoic acid) and trans-2-nonenal (nonenal), Sigma-Aldrich (MO, USA) (see Table 3.2). Octanoic acid was selected to represent more polar odorous compounds while nonenal represents less polar odorous compounds. Dodecane (Eastman Organic chemicals (NY, USA) was used as an internal standard to normalise data for a calibration curve which was intended to be the basis for data analysis and discussion of results. This was aimed at correcting the possible loss of analytes during sample preparation or sample inlet. Dichloromethane (40-50 ppm amylene, ACS reagent, 99.5%), Sigma-Aldrich (ON, Canada) was used as a solvent. A stock of solution was prepared by adding nonenal (0.1 g), octanoic acid (0.1 g) and dodecane (0.2 g) into a 10.0 mL up to volume by adding dichloromethane.

The stock solution was stored in the fridge (4 ^{o}C) throughout the experiment. When needed it was taken out of the fridge, shaken for 30 seconds and allowed to sit for at least 1 minute to thaw before inoculation. Fabrics were laid flat in sterile empty Petri dishes and covered prior to inoculation as shown in Figure 3.1. A volume of 10 μL of octanoic acid-nonenal solution was directly inoculated onto the swatches with a needle and the fabric was covered immediately with the Petri dish lid. The inoculated fabric was allowed to sit to allow the solvent to evaporate for 24 hours. Fabric specimens designated for "no washing" were folded once and then placed into a crimp top 20 ml vial (23 x 75mm) and the mouth immediately capped with a tin plate seal (8mm hole, 20mm PTFE/BUTYL rubber) (Chromatographic Specialties, ON, Canada). The "no wash" specimens were then prepared for headspace and direct extraction as described below. Specimens designated for washing were left in the Petri dishes and prepared for washing.

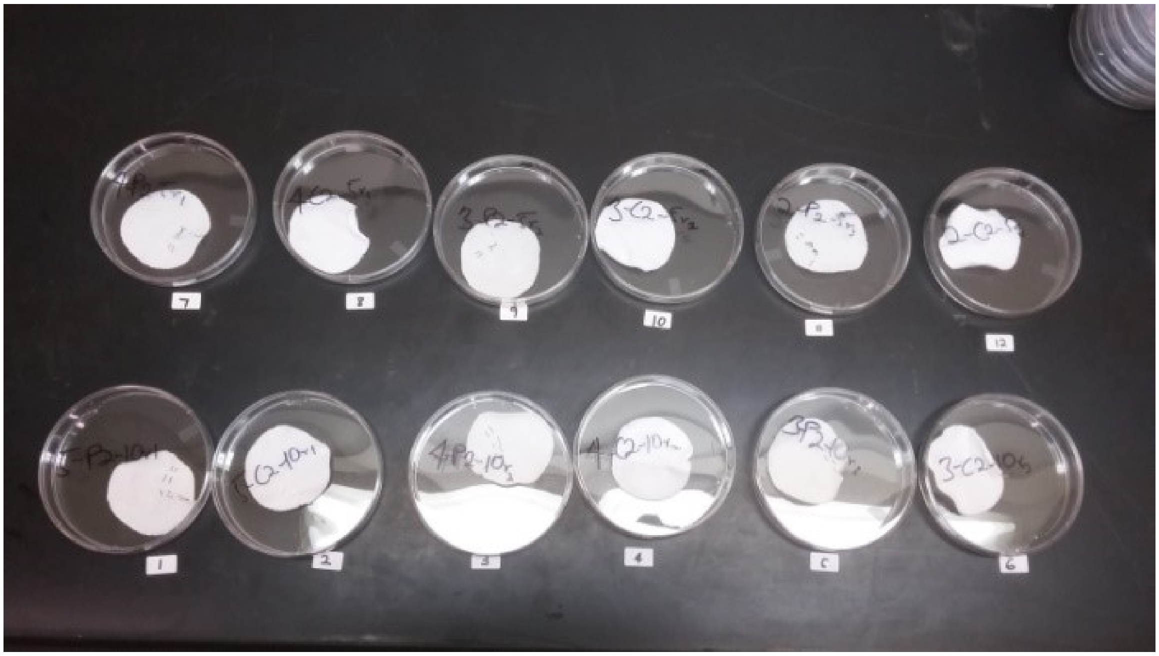


Figure 3.1 Fabric samples laid in Petri dishes

3.1.3 Laundering

The test method for colourfastness was adopted with some modification using the Launder-O-meter (CAN/CGSB-4.2 No. 19.2-2003/ ISO 105-C06:1994). Details of changes are sown in Appendix B. Two separate washing liquor solutions were prepared in a 10 L flask with either Tide® Free and Gentle Liquid detergent (regular) or Tide® Plus Febreze Sport Liquid detergent (sport) and the temperature raised to 30 ^{o}C. A siphoning apparatus was used to siphon 450 ml of liquor solution into a canister (Figure 3.2). The inoculated fabric specimen and 10 steel balls were then added and the canister (Figure 3.3) was capped. The water bath temperature of Launder-O-meter was raised to 30 ^{o}C. All canisters containing liquor and fabric specimens were screwed in place on the rack inside the washing machine. Washing was carried out for 10 minutes where the canisters were shaken at 40 ± 2 rotations/minute.

After removing the canisters from the machine, the fabric and the steel balls were collected in a sieve as the washing liquor was poured away. While in the sieve, the fabric specimen was rinsed under running water from the tap for 30 seconds on each side of the fabric as shown in Figure 3.4. Immediately, the fabric was removed from the sieve using tweezers and rinsed again in 3 different flasks full of fresh water while shaking by hand for 30 seconds each. A clean paper towel was used to soak some of the water from the fabric specimen before it was hung to air dry in a fume hood (Figure 3.5). Fabric specimens were allowed to air dry in a fume hood for 22 hours.

Control fabrics were introduced to detect any cross-contamination that may occur during inoculation, washing and drying processes. Cotton and polyester fabrics were prepared as the main specimens in Petri dishes and placed in line with the main specimens during inoculation without any solution spiked on them. They were washed in separate canisters and dried on the same line as the main specimens. Chemical analyses were conducted as described below.

Figure 3.2 A wash stock solution with a siphoning apparatus

Figure 3.3 Canisters filled with wash solution and steel balls

Figure 3.4 Rinsing of fabric samples directly from tap water

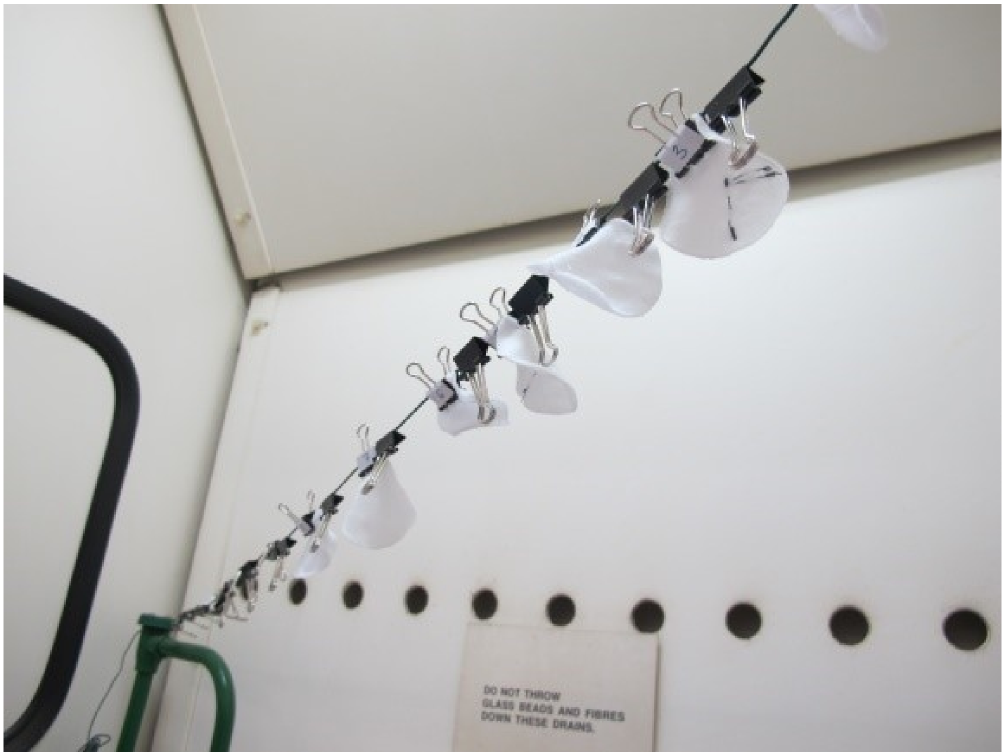


Figure 3.5 Drying of samples on a line in clean fume hood

3.2.4 Inoculation/wash cycles

The process from inoculation to drying was completed once for 1 inoculation/wash cycle, repeated 5 times in total for 5 inoculation/wash cycles and 10 times for 10 inoculation/wash cycles before chemical analysis was carried out. Three replicates for each inoculation/wash cycle were performed.

3.2.5 Headspace analysis using Solid Phase Micro-Extraction Fibre (SPME)

Headspace analysis was conducted to simulate the volatiles released when body odour is formed in clothing before washing. SPME fibres used in the study had a “tri-mode” divinylbenzene/carboxoen/polydimethylsiloxane (DVB/CAR/PDMS) extraction phase (SUPELCO, PA). After drying, fabric samples ready for analysis were folded once and placed in a 20 mL vial before crimp-capping with a clamp. The SPME fibre was thermally cleaned for 3 minutes at 250 ^{o}C under a flow of 1.5 mL/min of 5.0-grade helium (Praxair, Edmonton, AB) before being inserted through the cap of the vial for exposure to volatiles. Extractions were conducted for 22 hours for 30 +- 1 ^{o}C with vials immersed in a temperature-controlled, stirred oil bath (Figure 3.6). The duration was chosen to fit the experimental schedule and differed by only one hour from 21 hours which was deemed the optimum time for SPME extraction of fabrics (Leidal et al., 1982; McQueen et al., 2014). The SPME fibre was removed from the vial and analytes immediately desorbed from the fibre in the GC inlet for 3 minutes. The instrument continued to run for another 29 minutes.

3.2.6 Direct extraction

Direct extraction was conducted to quantify odorants still remaining in the fabrics following washing. While the SPME fibre was inside the inlet, the 20 ml vial was uncapped and 18 ml of dichloromethane was added to the fabric specimen inside the vial and capped again. The vial was left to sit for at least 30 minutes with handshaking for the first 2 minutes, after 10 minutes (for 2 minutes) and for the final 2 minutes. The vial was uncapped, the fabric was

Figure 3.6 Extraction of volatiles from fabric samples in a vial immersed in oil-bath using SPME fibre

squeezed with tweezers against the inner wall of the vial to extract as much of the odorants as possible and removed from the vial. Following this, 1 g of anhydrous sodium sulfate (Na_2SO_4) was added to the remaining solution, shaken. Two more grams of Na_2SO_4 was added to capture any excess water in the solution and left to sit for 2 minutes. Fifteen millilitres of the dried solution was collected and transferred into a Kuderna – Danish (K-D) column evaporator for concentration.

3.2.7 Concentration

The K-D column evaporator (500 ml reservoir, 15 ml conical receptor, and 3-ball Snyder column, 24/45 joint) was used at a controlled temperature of 60 ^{o}C for the concentration as was used in previous research (Lee, Papathakis, Feng, Hunter, & Carr, 1991; Velfgek et al., 1978). A 2 L container was filled with water with a Snyder column stationed just above the water. The bottom part of the concentrator was immersed half way inside the water. Then the mouth of the container and the bottom part of the concentrator were wrapped with aluminum foil before the temperature was raised to 60 ^{o}C (see Figure 3.7). The 15 ml of dried solution was put inside the Snyder column. As the solution boiled and the dichloromethane evaporated, the odorants from the fabric were being concentrated. When the remaining solution reached the 1 ml mark on the column, the column was unscrewed, taken out of the water and placed back in to slow the concentration down so it could be more closely monitored. The column was removed when the concentration reached 200 µl and transferred into a 1 ml interlocked GC vial. Using a 10 µl needle, 1 µl was injected into the GC for analysis of odorants extracted from the fabric specimen.

3.2.8 Gas Chromatography/Flame Ionization Detection (GC-FID)

GC-FID is an instrument known to be used for the identification and quantitation of volatile and semi-volatile organic compounds in complex mixtures and also for determination of molecular weights (Hites, 1997). This powerful instrument was employed in identifying peaks of odorants from the headspace as well as the direct extraction of textile materials in previous studies (e.g., Richter, Bremer, Silcock, & Laing, 2017; McQueen et al., 2014, Curran et al., 2010).

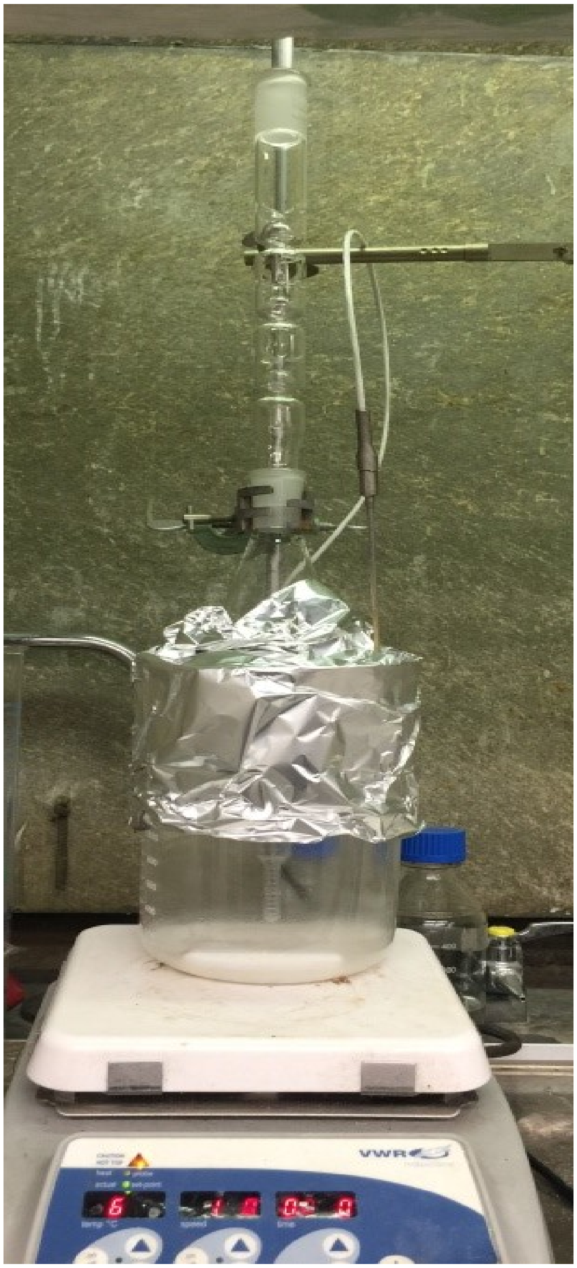
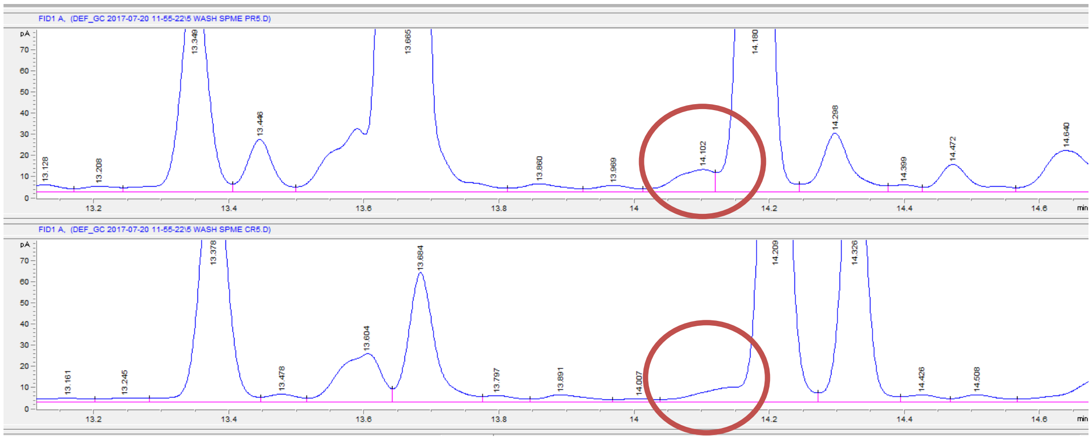


Figure 3.7 Kuderna-Danish evaporator prepared for concentration of directly extracted odorants from fabric samples

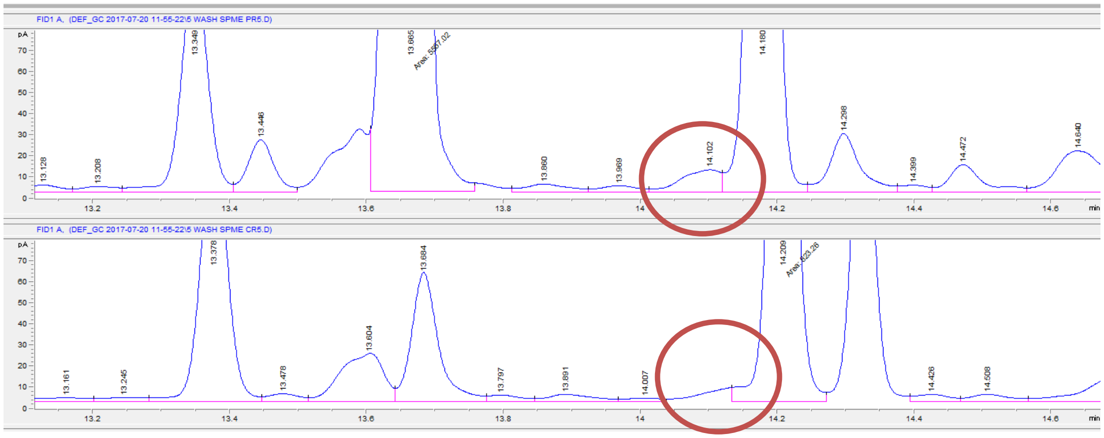
The samples were analyzed using GC-FID, with 30 m x 0.53 mm column with 1 um film thickness Rxi®-5MS (Crossbond® 5% diphenyl/95% dimenthyl polysiloxane) Rxi®-5MS (Chromatographic Specialties Inc., ON, Canada). Helium (5.0 grade; Praxair, Edmonton, AB) as the carrier gas (flow rate: 3.3 mL⁄min) was used for the separation and analysis of the analytes. The analytes for both headspace (volatiles) and direct extraction (liquid) were desorbed or injected respectively, into the split/splitless injection port of the GC in a splitless mode using an inlet temperature set at 250 ^{o}C. A Sky^{TM} Liner, SPME (0.75mm x 6.35 x 78.5) for Agilent GCs was used for headspace analysis and Sky^{TM} Liner, Splitless, single taper gooseneck wool (4mm x 6.35 x 78.5) for Agilent GCs (Chromatographic Specialties Inc., ON, Canada) was used for direct extraction. The oven of GC was held at an initial temperature of 50 ^{o}C, followed by a ramp up to 10 ^{o}C/minute to 240 ^{o}C/minute and held for 10 minutes. The total run was 32 minutes in total. The minimum peak width was set at 200 Hz/0.001min.

3.3 Data analysis

The peak area of each headspace sampling and direct extraction of fabrics was recorded after each run of the GC instrument. After the automatic integration by the system, manual integration was also done to make sure all peak widths were consistent, as some peaks were integrated beyond their peak widths as shown in Figure 3.8. The peak areas of odorants were not always consistent with the increase or decrease of internal standard (dodecane) (see Figure 3.9). For example, as dodecane increased, octanoic acid would decrease, and when dodecane decreased, octanoic acid would increase. Therefore, instead of normalizing data based on the dodecane internal standard, the data was normalized by dividing the original peak areas of odorants by the weight of cotton (0.46 g) or polyester (0.44 g). The averages of the 3 replicates were then used for data analysis and discussion. Calibration curves were calculated for octanoic acid and nonenal, (the results of which are shown in Appendix C). However, these calibration curves were not used in the current study due to the inconsistency associated with the internal standard.



a. Automatic integration showing the bottom peak stretching from 14.007 mins to 14.3 mins instead of breaking at 14.102 as the top peak



b. Manual breaking of the bottom at 14.102 mins

Figure 3.8 Integration of peaks

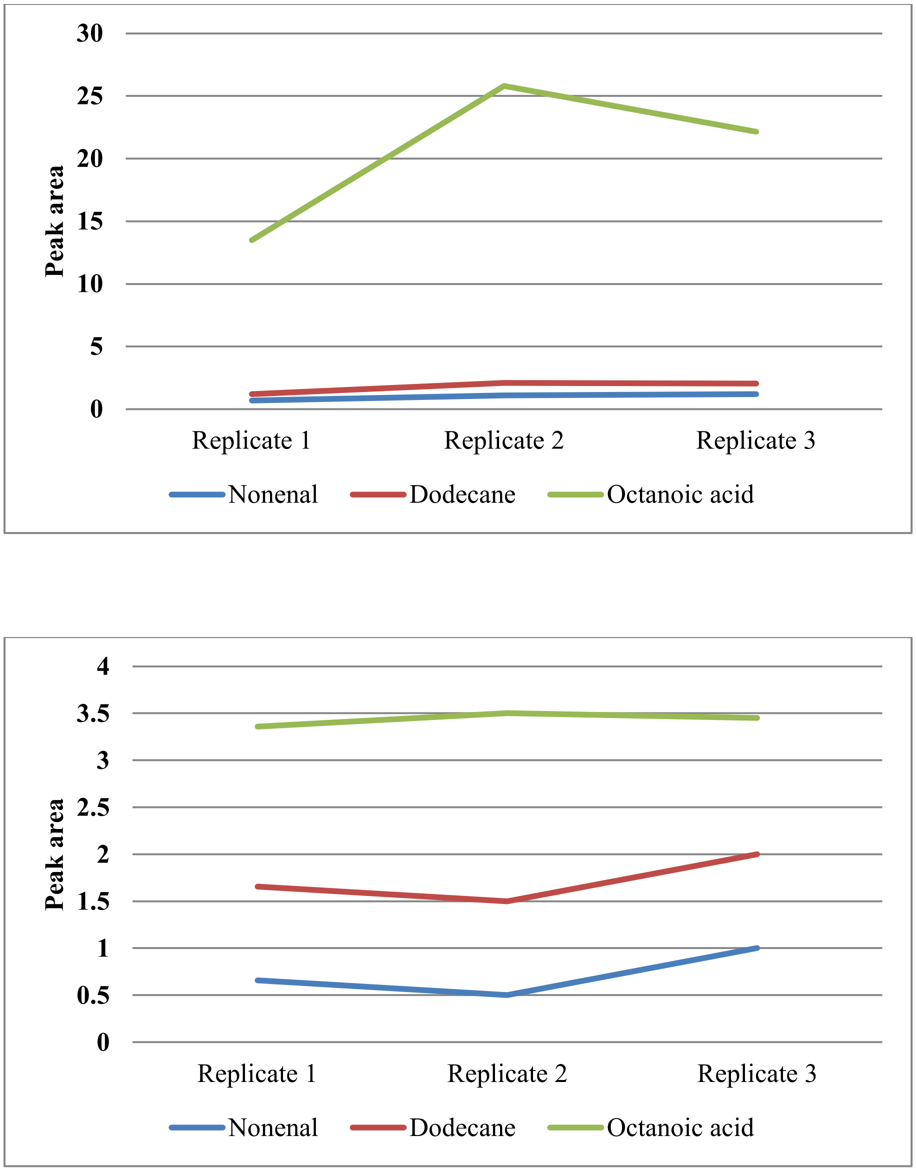


Figure 3.9 Examples of normalizing peak areas of standards using dodecane.

3.3.1 Statistical analysis

Descriptive statistics were calculated (i.e. mean, standard deviation etc.). Graphs showed the peak heights of odorants for each wash level with regular and sport detergent of cotton and polyester. A $\log_{10}$ transformation of the data was also carried out to make meet the highly skewed data less biased. Octanoic acid and nonenal were analyzed separately since only the peak area was measured and not the concentration. For octanoic acid, cotton and polyester fabrics were analyzed together since the log-transformed data was less skewed. Therefore, for octanoic acid, a 3-way analysis of variance (ANOVA) was carried out with fabrics, detergents and wash cycles as the factors. For the nonenal data, when cotton and polyester were assessed for normality, a bi-modal distribution was apparent, so the cotton and polyester were significantly different. Therefore, each fabric was separately analysed using a double 2-way ANOVA with detergent and wash level as the factors. Where there was any significant effect among main effects and interactions between more than two levels, a Tukey's Honestly Significant Difference post-hoc test was conducted. All statistical analysis was completed using IBM SPSS statistics 25 software.

3.4 Preliminary testing

3.4.1 Retention times

Individual compounds (octanoic acid, nonenal, dodecane) were dissolved to 1000 mg/mL in dichloromethane and 1 μl of each was injected separately into the GC instrument to determine their retention times shown in Table 3.3. All compounds were then mixed together in one solution to simulate real body odour, as body odour is a mixture of different odorous compounds. One microliter of the mixed solution was injected into the GC which showed that the retention times of odorants in the mixed solution were not different from their separate retention times. Therefore the retention times of odorants were used for data collection.

3.4.2 Storage

Storage of inoculated samples was tested to explore the possibility of storing inoculated samples in the freezer in order to wash them when needed during the experiment. Ten microliters (10 µl) of the stock solution was inoculated onto four sets of cotton specimens. One was extracted immediately; the second set was frozen and extracted after 2 days, the third after one week and the fourth after 2 weeks of freezing. The result shown in Figure 3.10 suggests that there is a huge change in odour intensity and it was concluded that storage would influence the results of the experiment considerably.

Table 3.3 Retention time for compounds separately and in solution (with other odorants)

Compound	Retention times (minutes)	
	Individual	In solution
Nonenal	13.6	13.7
Dodecane	14.2	14.2
Octanoic acid	15.6	15.8

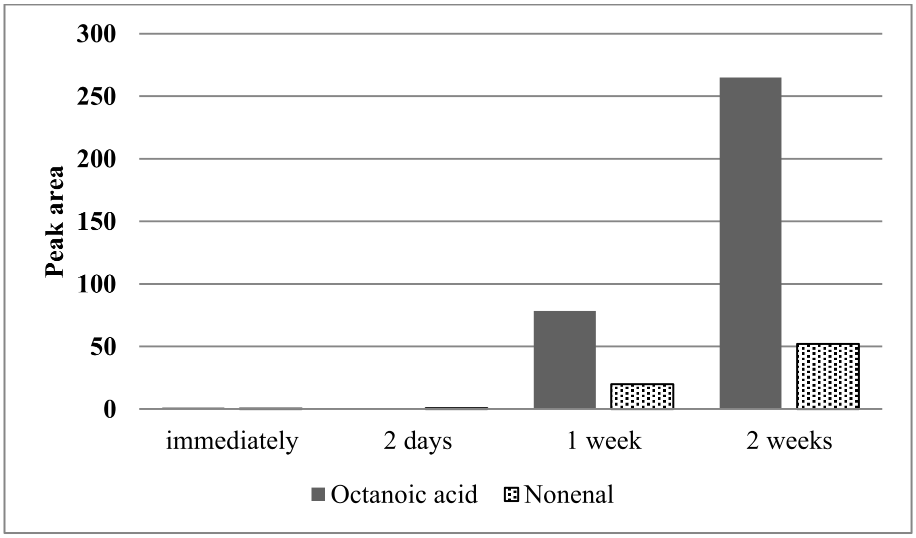


Figure 3.10 Headspace analyses of frozen samples

Chapter 4

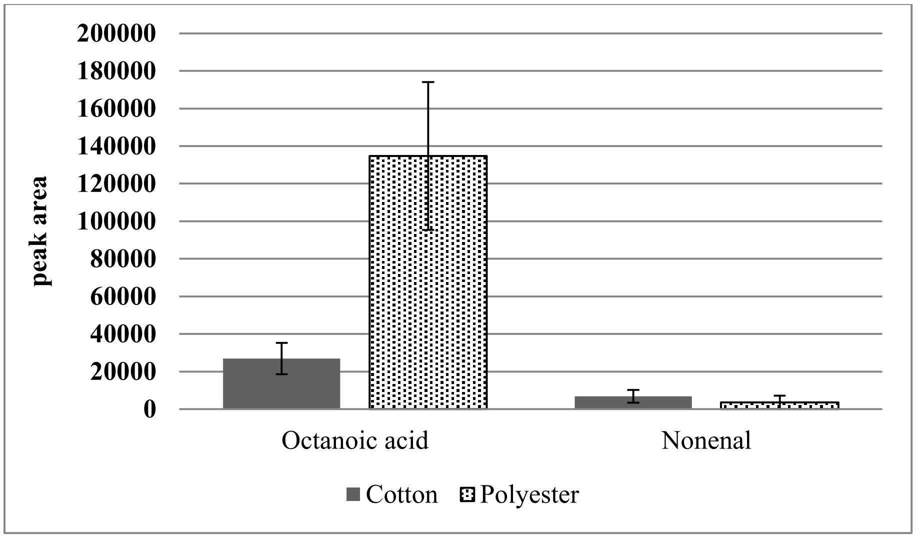
Results

4.1 Initial sorption of odorants in cotton and polyester fabrics

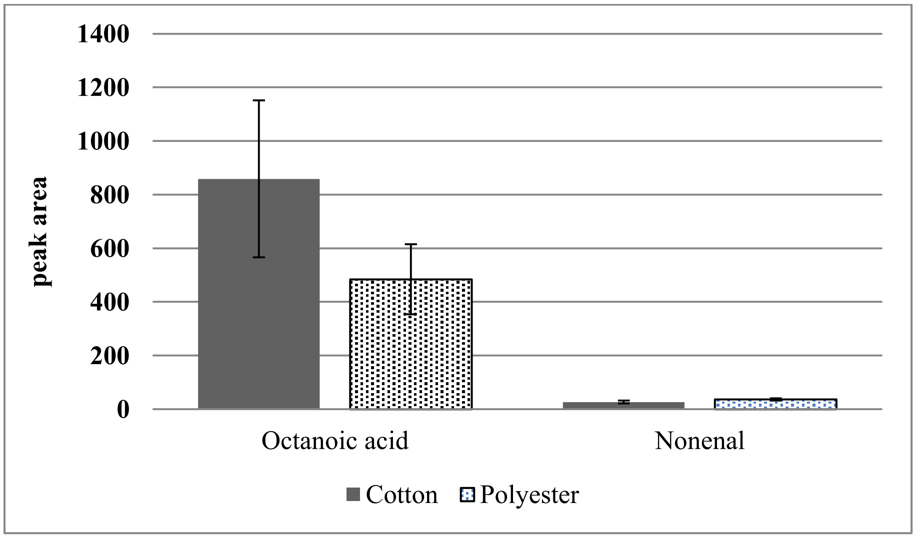
Figure 4.1 shows the original peak areas of octanoic acid and nonenal released in the head-space (i.e., SPME) (4.1a) and directly extracted (4.1b) from cotton and polyester fabrics prior to washing. Headspace peaks of octanoic acid were much lower for cotton fabric (26897.03 ± 8316.47) than for polyester (134743.14 ± 39373.20). The same result was obtained for nonenal (cotton =6810.00 ± 3458.00; polyester =15717.00 ± 3567.00) even though the difference was not as large (see Table 4.1). In addition, the peak areas for octanoic acid desorbed by both fabrics were substantially greater than the peak areas of nonenal (cotton: 6810.00 ± 3458.00; polyester: 15717.00 ± 3567.00). In direct extraction, the peak height of octanoic acid directly extracted from cotton was higher than from polyester. However, the peak height of nonenal directly extracted from cotton was lower than polyester. Regardless of the fibre type, the peak heights of octanoic acid extracted are considerably higher than nonenal.

4.2 Reduction in odorous compounds following one wash

The percentage of odorants quantified from fabric samples that had been inoculated and then washed once compared to the amount of odorants desorbed and directly extracted from unwashed samples was calculated and is shown in Figure 4.2. Laundering was successful in removing a significant amount of odorants from the fabrics. A large amount of octanoic acid was removed from cotton as there was 98.0 % reduction of octanoic acid volatiles in the headspace after one wash. Moreover, 99.6 % and 98.6 % reduction in octanoic acid compounds from cotton was achieved with regular detergent and sport detergent respectively. In addition, 95% of octanoic acid present in the headspace of unwashed polyester was removed by laundering while 86.2% (regular detergent) and 76.2% (sport detergent) were removed considering direct extraction from the polyester fabric. For nonenal, about 97.0% of volatiles in headspace present



a. Headspace

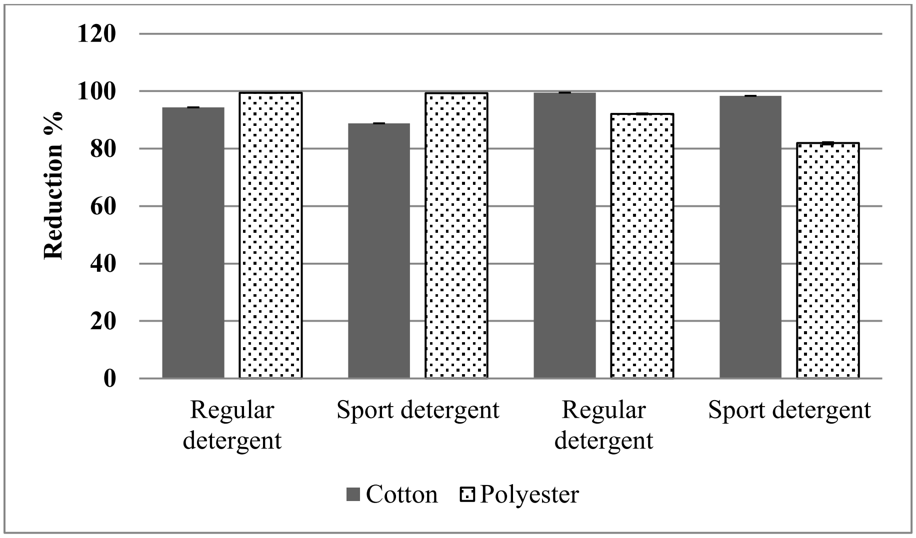


b. Direct extraction

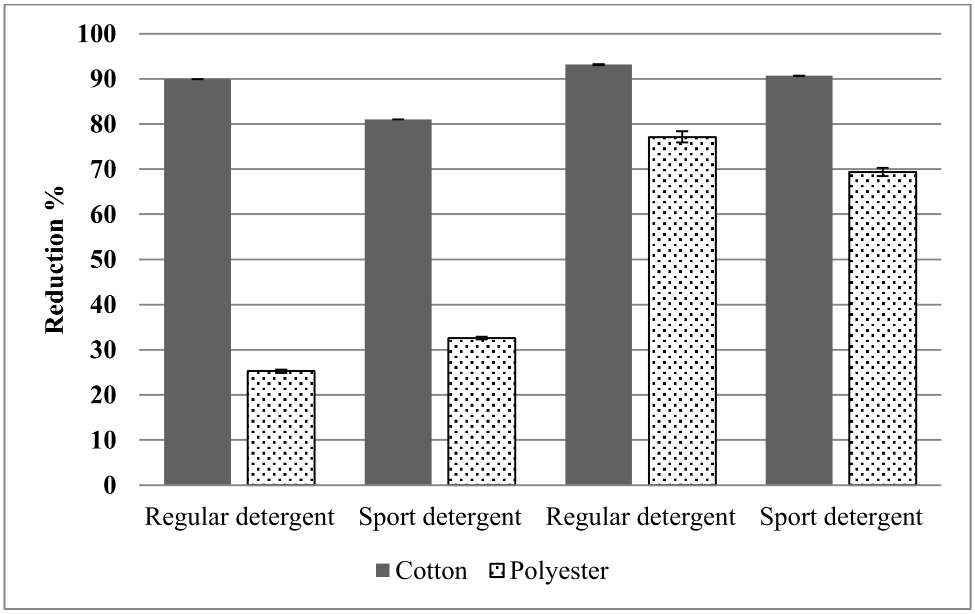
Figure 4.1 Initial sorption and desorption of odorants by cotton and polyester after inoculation without washing.

Table 4.1 Peak area of octanoic acid and nonenal for head-space sampling and direct extraction (with dichloromethane) from cotton and polyester fabrics following washing.

		Octanoic acid						Nonenal					
		Cotton			Polyester			Cotton			Polyester		
	Wash level	$\bar{x}$	sd	c.v%	$\bar{x}$	sd	c.v%	$\bar{x}$	sd	c.v%	$\bar{x}$	sd	c.v%
Detergent	Direct extraction												
Regular	0	858.90	292.23	34	484.44	130.44	27	26.56	5.06	25	36.54	4.25	10
	1	3.71	0.60	16	66.73	22.61	34	1.55	0.55	36	15.00	5.32	35
	5	15.36	2.68	17	152.60	28.98	19	2.16	0.43	20	47.88	6.73	14
	10	8.36	1.08	13	147.86	66.24	45	1.29	0.93	72	37.50	22.36	60
Sport													
	1	11.64	0.55	5	115.46	46.51	40	2.11	0.26	12	14.68	4.91	27
	5	40.40	12.59	31	226.82	66.00	29	0.16	0.57	26	48.45	24.88	51
	10	25.99	10.22	39	163.53	34.37	21	2.28	0.71	31	43.67	11.45	26
	Headspace												
Regular	0	26897.03	8317.47	31	134743.14	39373.20	29	6810.00	3458.00	51	15717.00	3567.00	23
	1	347.65	40.60	12	613.89	177.09	29	149.00	29.72	20	8691.80	1378.10	16
	5	763.61	399.54	52	495.86	97.95	20	290.00	128.02	45	17266.72	4096.13	24
	10	291.13	60.90	21	660.35	70.71	11	178.43	42.05	24	18188.24	4087.40	22
Sport													
	1	495.98	69.40	14	561.31	78.43	14	201.50	5.01	3	5261.58	1161.45	22
	5	405.19	124.06	31	573.57	74.09	13	135.30	42.53	31	14115.18	9148.41	65
	10	327.28	116.58	36	585.37	86.63	15	200.05	66.98	33	12410.04	2685.37	22



a. Octanoic acid



b. Nonenal

Figure 4.2 Percentage (with error bars) of original odorants removed from textile fabrics after one inoculation/wash cycle

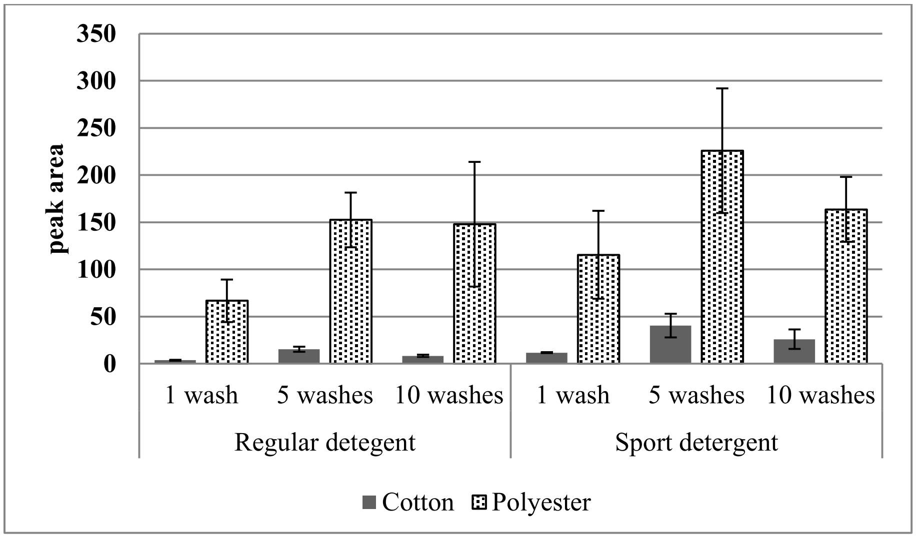
on unwashed cotton were removed after one wash, while only 44.7% (regular) and 66.5% (sport) was removed in the headspace from polyester. For direct extraction, at most 6.0% (regular) and 8.0% (sport) of the amount of nonenal was extracted from washed cotton. On the other hand, about 40% of nonenal was extracted from washed polyester.

4.3 Comparison of fabrics in the direct extraction of octanoic acid and nonenal

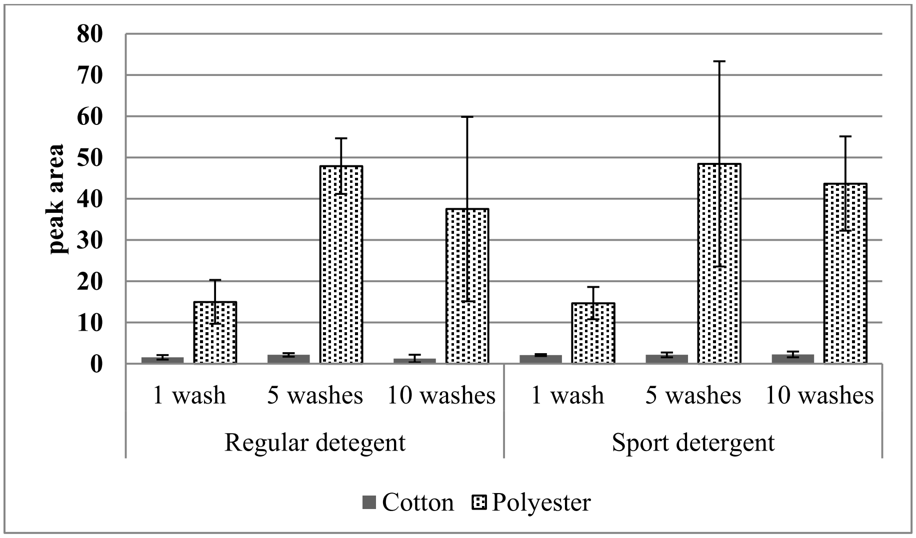
4.3.1 Octanoic acid

Figure 4.3a shows the peak areas of octanoic acid extracted from cotton and polyester after 1, 5 and 10 inoculation/wash cycles. There are clear differences between the results for cotton and polyester. Cotton peaks were much lower than those for polyester at all wash levels for both detergents. Moreover, cotton peaks after one inoculation/wash cycle with the regular detergent were lower than for 5 and 10 cycles while the peak for 5 cycles was higher than for 10 cycles. With the sport detergent, the mean peaks for one wash were lower than those for 5 and 10 inoculation/wash cycles but there was no difference between 5 and 10 cycles. Overall, for the fabrics laundered using the sport detergent, peak areas were larger than those washed by the regular detergent at all inoculation/wash cycles. For polyester, however, while peaks for one cycle washed with regular detergent were lower than for 5 wash cycles, there appeared to be no difference between 5 and 10 inoculation/wash cycles. In addition, there was no difference in peak heights between polyester samples washed with sport and those washed with regular detergent.

Analysis of variance (ANOVA) results of direct extraction analysis of octanoic acid against fabrics, detergents and number of washes are shown in Table 4.2. There was a significant effect due to fibre type ($F_{1, 24}$ =536.77, $p \leq 0.001$) and due to the type of detergent used ($F_{1, 24}$=50.83, $p \leq 0.001$). Another main effect in the amount of octanoic acid directly extracted was due to the number of inoculation/wash cycles ($F_{2, 24}$ =37.97, $p \leq 0.000$). There was also a significant interaction for fabric with detergent ($F_{1, 24}$ =12.28, $p \leq 0.000$). However, no other interactions



a. Octanoic acid



b. Nonenal

Figure 4.3 Effects of variables on the direct extraction (with dichloromethane) of odorants from cotton and polyester fabrics

Table 4.2 Significance of variables affecting direct extraction of octanoic acid - ANOVA ($\log_{10}$ transformed) (n=3)

Source	df	SS	MS	F	P<
Fabric	1	9.00	9.00	536.77	0.000
Detergent	1	0.85	0.85	50.83	0.000
Number of washes	2	1.27	0.64	37.97	0.000
Fabric/Detergent	1	0.21	0.21	12.28	0.000
Fabric/Washes	2	0.08	0.04	2.48	NS
Detergent/Washes	2	0.02	0.01	0.51	NS
Fabric/Detergent/Washes	2	0.01	0.01	0.32	NS
Error	24	0.40	0.02		

NS is Non-significant at p>0.05

Table 4.3 Significant differences of variables direct extraction of octanoic acid from fabrics. Tukey range tests

Source	Mean	n	Tukey groupings
Wash			
1	1.37	12	]
10	1.66	12	]
5	1.82	12	]
Fabric/Detergent			
Cotton/Regular	0.89	9	
Cotton/Sport	1.34	9	
Polyester/Regular	2.04	9	]
Polyester/Sport	2.20	9	]

Means grouped by vertical lines are not significantly different at $p \leq 0.05$ level.

involving fibre and the number of inoculation/wash cycles or detergent and wash cycles were found to be significant.

Further, post hoc analysis (Table 4.3) showed that the number of washes had a significant effect on the amount of octanoic acid directly extracted from cotton and polyester as wash cycles 1 results ($\bar{x}$ =1.37), 5 ($\bar{x}$ =1.82) and 10 ($\bar{x}$ =1.66) were significantly different from each other. Table 4.3 also shows that the amount of octanoic acid extracted from cotton fabrics washed with regular and sport detergents were all significantly lower than from polyester samples. Moreover, results for cotton fabrics washed with the regular detergent ($\bar{x} = 0.89$) were significantly different from cotton fabrics washed with the sports detergent ($\bar{x} = 1.34$). In addition, polyester fabrics washed with the regular detergent ($\bar{x} = 2.04$) were not significantly different from the polyester fabrics washed with sports detergent ($\bar{x} = 2.20$).

4.3.2 Nonenal

Nonenal peaks for cotton and polyester are shown in Figure 4.3b. A large difference between results for cotton and polyester fabrics at all wash cycles, with both the regular and sport detergents, is apparent. Cotton peaks are considerably lower (ranging from a mean of 1.29 to 2.28) than polyester peaks (ranging from a mean of 14.68 to 48.45) across all inoculation/wash cycles.

ANOVA results in Table 4.4 presents the variables that have significant effects on the direct extraction of nonenal from cotton (4.4a) and polyester (4.4b). The distribution of means for cotton and polyester were different. Interestingly, the number of washes for cotton was not significant ($F_{2,\,12} = 0.81$; $p \leq 0.01$) but it was significant for polyester ($F_{2,\,12} = 0.88$ $p \leq 0.001$). However, the detergents used did not have any significant difference on both cotton and polyester ($F_{1,\,12} = 2.41$, $F_{1,\,12} = 0.14$; $p \leq 0.01$, respectively). Post hoc analysis (Table 4.5) showed that there was no significant difference between 5 ($\bar{x} = 1.66$) and 10 ($\bar{x}$

Table 4.4 Significance of variables affecting direct extraction of nonenal from cotton and polyester- ANOVA (log$_{10}$ transformed)

(n=3)

a. Cotton

Source	df	SS	MS	F	P<
Number of washes	2	0.10	0.05	0.81	NS
Detergent	1	0.14	0.14	2.41	NS
Washes/Detergent	2	0.12	0.06	1.01	NS
Error	12	0.71	0.06		

NS is Non-significant at p>0.05

b. Polyester

Source	df	SS	MS	F	P<
Number of washes	2	0.88	0.44	14.57	0.001
Detergent	1	0.004	0.004	0.14	NS
Washes/Detergent	2	0.02	0.01	0.27	NS
Error	12	0.36	0.03		

NS is Non-significant at p>0.05

Table 4.5 Significant differences of variables direct extraction of nonenal from polyester (Tukey range tests)

Source	Mean	n	Tukey groupings
Wash			
1	1.16	6	
10	1.57	6	]
5	1.66	6	]

Means grouped by vertical lines are not significantly different at $p \leq 0.05$ level.

$= 1.57$) washes of polyester fabrics but shows a significant difference between 1 ($\bar{x} = 1.16$) and 5 and between 1 and 10 cycles.

4.4 Comparison of fabrics in headspace sampling of octanoic acid and nonenal

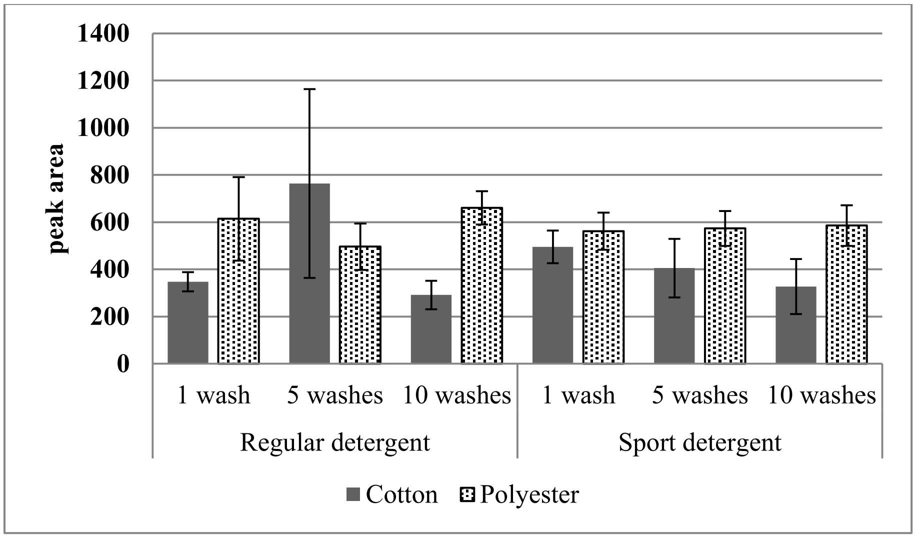
4.4.1 Octanoic acid

In general, the octanoic acid detected in the headspace was higher from polyester fabrics than from cotton fabrics (see Figure 4.4a). There were some exceptions to this, for example, after 5 inoculation/wash cycles with regular detergent, the average peak area for cotton was 763.65 and for polyester was 495.86. There appeared to be minimal differences in the quantity of octanoic acid emitted into the headspace depending on the detergent type used and the number of inoculation/wash cycles. It also showed that while peaks of cotton seem to decrease from 1 to 10 inoculation/wash cycles with sport detergent, peaks of octanoic acid removed from polyester was constant.

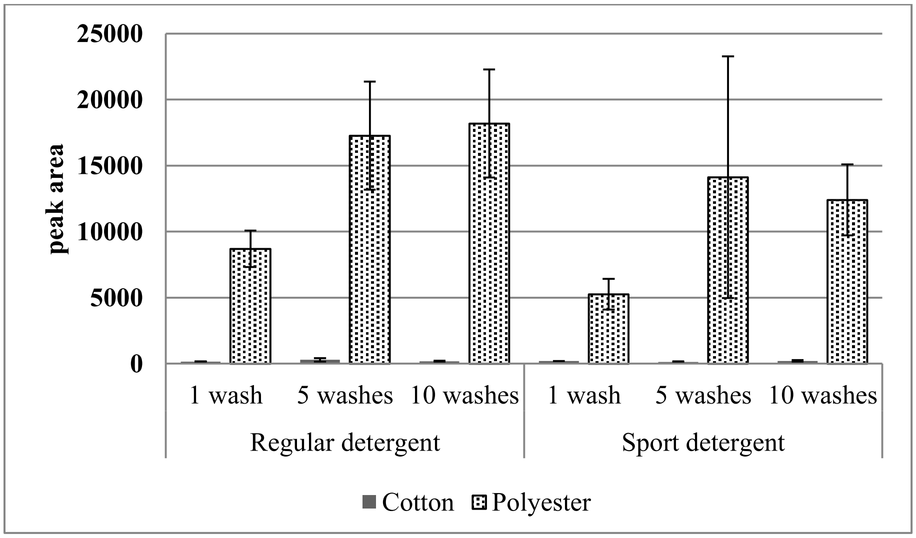
Table 4.6 shows ANOVA results of headspace analysis of octanoic acid against fabrics, detergents and number of washes. It shows significant differences exist between cotton and polyester ($F_{1,24}$ =16.09, $p \leq 0.001$). Also, within each fabric type, there were differences between wash cycles ($F_{1,24}$ =5.17, $p \leq 0.01$). Further post hoc analysis revealed that there was a significant difference between 5 inoculation/wash cycles ($\bar{x} = 2.71$) and 10 cycles ($\bar{x} = 2.48$) of cotton samples as shown in table 4.7. In addition, cotton also differed significantly from polyester ($\bar{x} = 2.80$) after 10 inoculation/wash cycles. There was also no significant effect in the quantity of octanoic acid emitted into the headspace for detergent, either as a main effect or an interaction.

4.4.2 Nonenal

Across all washes and between both the regular and sport detergents, nonenal peaks from cotton were much lower than from polyester as shown in Figure 4.4b. However, cotton average peaks for regular detergent had marginal differences between 1 ($\bar{x} = 148.98$, ± 29.72), 5 ($\bar{x} = 287.46$ ±



a. Octanoic acid



b. Nonenal

Figure 4.4 Effects of variables on the headspace sampling of odorants from cotton and polyester at all wash levels

Table 4.6 Significance of variables affecting headspace sampling of octanoic acid - ANOVA ($\log_{10}$ transformed)
(n=3)

Source	df	SS	MS	F	P<
Fabric	1	0.22	0.22	16.09	0.001
Number of washes	2	0.04	0.02	1.61	NS
Detergent	1	0.001	0.001	0.08	NS
Fabric/Wash	2	0.14	0.07	5.17	0.01
Fabric/Detergent	1	0.00	0.00	0.02	NS
Wash/Detergent	2	0.03	0.07	1.20	NS
Wash/Fabric/Detergent	2	0.10	0.05	3.73	NS
Error	24	0.33	0.01		

NS is Non-significant at p>0.05

Table 4.7 Significant difference variables affecting the headspace sampling of octanoic acid on fabrics. (Tukey range tests)

Source	Mean	n	Tukey groupings
Fabric/wash			
Cotton/10	2.48	6	│
Cotton/1	2.62	6	│ │
Cotton/5	2.71	6	│
Polyester/5	2.72	6	│
Polyester/1	2.76	6	│
Polyester/10	2.80	6	│

Means grouped by vertical lines are not significantly different at $p \leq 0.05$

128.02) and 10 ($\bar{x} = 178.43 \pm 42.05$) cycles, but between 5 and 10 cycles there was a noticeable difference. Moreover, for sport detergent there was an apparent difference between cotton samples at all wash cycles. Regular detergent peaks for polyester were generally higher when compared with sport detergent peaks (Table 4.1).

Table 4.8 shows ANOVA of effects of variables affecting headspace sampling of nonenal from cotton (4.8a) and polyester (4.8b). Interestingly, Table 4.8a shows that number of washes and detergents had no effect on cotton ($F_{2,\,12} = 0.11$; $F_{1,\,12} = 0.48$, $p \leq 0.001$ respectively). However, the number of washes was shown to be significant in the removal of nonenal from polyester ($F_{2,\,12} = 11.72$, $p \leq 0.001$). In addition, post-hoc analysis in table 4.9 showed a significant difference between 1 ($\bar{x} = 3.82$) and 5 ($\bar{x} = 4.16$) and between 1 and 10 ($\bar{x} = 4.17$) inoculation/wash cycles.

Table 4.8 Significance of variables affecting headspace sampling of nonenal from cotton and polyester- ANOVA ($\log_{10}$ transformed)

(n=3)

a. Cotton

Source	**df**	**SS**	**MS**	**F**	**P<**
Number of washes	2	0.004	0.002	0.11	NS
Detergent	1	0.01	0.01	0.48	NS
Washes/Detergent	2	0.17	0.83	4.52	NS
Error	12	0.22	0.018		

NS is Non-significant at p>0.05

b. Polyester

Source	**df**	**SS**	**MS**	**F**	**P<**
Number of washes	2	0.464	0.23	11.72	0.002
Detergent	1	0.137	0.14	6.95	NS
Washes/Detergent	2	0.006	0.003	.144	NS
Error	12	0.237	0.02		

NS is Non-significant at p>0.05

Table 4.9 Significant differences of variables affecting headspace sampling of nonenal from polyester (Tukey range tests)

Source	Mean	n	Tukey groupings
Wash			
1	3.82	6	
5	4.16	6	]
10	4.17	6	]

Means grouped by vertical lines are not significantly different at p ≤ 01 level.

Chapter 5

Discussion

5.1 Initial sorption of odorous compounds in unwashed fabrics

5.1.1 Direct extraction of compounds from fabrics

Cotton has numerous hydroxyl groups (OH) on its cellulosic polymer that makes it hydrophilic (Kadolph, 2010; McQueen et al., 2008). Whereas, nonenal is hydrophobic and oily in nature and may have a good affinity to the olephilic polyester fibres (Obendorf & Webb, 1987; Obendorf, Namaste, & Durnam, 1983). Munk et al (2001) inoculated six different odorants, including octanoic acid and nonenal, onto cotton and polyester fabrics and extracted the compounds 24 hours later using dichloromethane. Their data suggest that octanoic acid extracts from cotton were higher than extracts from polyester. Similarly, Bowers and Chantrey (1969) also found polyester to absorb and retain larger amounts of sebum (a hydrophobic secretion) from the human body.

My research confirms that sorption of odorants by textile fabrics are clearly influenced by the chemistries of odorous compounds and the type of textile materials. The present research findings are similar to the findings from previous studies; cotton sorbed greater amounts of octanoic acid compared with polyester and polyester sorbed greater amounts of nonenal compared with cotton (Figure 4.1a). These findings, that more nonenal was directly extracted from polyester than from cotton were expected. Cotton may have allowed more sorption of octanoic acid into the fibre structure due to its large number of polar sites for the formation of hydrogen bonds.

5.1.2 Headspace analysis of compounds emitted from fabrics

Desorption of odorants by textile materials is likely also influenced by the chemistries of both odorants and textile materials, although the mechanisms that are involved are much less clear. Cotton fabrics desorbed much lower quantities of both octanoic acid and nonenal than polyester did, as was evident in the total peak areas of desorbed odorants following headspace analysis (Figure 4.1b). The numerous hydroxyl groups (OH) on the cellulosic polymer would allow cotton to absorb more octanoic acid into the fibre structure through the formation of hydrogen bonds. This can lead to the trapping of odorous compounds within the fibre structure, resulting in the lower emission of the odorants by the fabric. Conversely, polyester is hydrophobic and olephilic (Obendorf et al., 1983), so the sorption of octanoic acid may have been mostly attached to the surface of polyester fibres, leading to a more rapid and higher desorption of odorants into the environment (headspace) than for cotton (Richter, Bremer, Silcock, & Laing, 2017; Hammer, Berner-Dannenmann, & Hoefer, 2013). Moreover, cotton has been found to have a low adsorption rate and was slow in the release of volatiles while polyester has higher adsorption rates and continuously desorbs volatiles over a long period of time (Richter et al., 2017).

In another study where SPME was used to collect volatiles from human hands onto sorbent textile materials using contact and non-contact sampling methods, polyester materials were shown to desorb a high amount of acids (Prada et al., 2011). The authors suggested that polyester could be able to trap acid compounds with hydroxyl groups which include octanoic acid more readily, but also releases them more readily due to its hydrophobicity and non-absorbency (Prada et al., 2011). Similar results were found by Hammer et al., (2013) when they inoculated isovaleric acid onto untreated wool, cotton and polyester materials. Using liquid scintillation counting after 3 hours and 20 hours of exposure, polyester was shown to release more isovaleric acid than cotton and wool did. This was attributed to the swelling differences between these fibres, as cotton swells to accommodate more liquid than both polyester and wool do (Hammer et al., 2013). In addition, cis-3-hexenyl salicylate and several aroma compounds were found to be smoothly distributed throughout cotton but patchy on polyester which was also attributed to the lower polarity of polyester (Liu et al., 2005). This could be the reason for the higher desorption rate of the carboxylic acid from polyester in the current study, compared with cotton.

The amount of nonenal desorbed into the headspace from cotton was also lower than volatiles released from polyester. Nonenal is hydrophobic and oily in nature and may have been attracted more to the olephilic polyester fibres than to cotton. Through the use of electron backscattered imaging of oily soils, other researchers have shown that penetration occurred in cotton fibre and not in polyester fibre (Obendorf & Webb, 1987; Obendorf, Namaste, & Durnam, 1983). Instead, oily soils adsorbed to the surface of the polyester fibres. In earlier research, other authors have found that as moisture regain increased, soiling decreased, which led to a hydrophobic and olephilic materials like polyester to sorb larger amounts of body sebum (an oily body excretion) (Bowers & Chantrey, 1969). This is evident in the higher amount of nonenal directly extracted from polyester in this study (Figure 4.1b).

As in previous studies, this study showed that more nonenal was released into the headspace from polyester than from cotton. In the Richter et al., (2017) research, polyester was found to exhibit a higher adsorption rate than cotton and was shown to continuously desorb volatiles over a longer period of time. This is similar to previous studies comparing the retention of odorants by textile materials (Munk et al., 2001). Munk et al., (2001) collected sweat samples on cotton and polyester swatches from human participants and found that aldehydes (including 2-nonenal) were more dominant in polyester odour profile than in cotton. However, Prada et al., (2011) found that aldehydes made up the majority of the compounds profiled from cotton fabrics following contact with the hands, whereas carboxylic acids dominated from polyester (Prada et al., 2011).

Furthermore, it is worth mentioning that the peak areas for nonenal were typically lower than for octanoic acid the majority of the time. The calibration curves shown in Appendix C (Figure C1& C2) indicate that for the same concentration, the total peak area for nonenal is much lower than for octanoic acid. However, for the head-space analysis above, inoculated/washed polyester fabrics, the nonenal total peak areas were larger than for those of octanoic acid. So although it was not possible to directly compare octanoic acid and nonenal in this study for head-space analysis, these higher total peak areas suggest that the amount of nonenal, desorbed from polyester, was far higher than octanoic acid (Figure 4.4).

5.2 Effect of laundering on the removal of odorants from fabrics

5.2.1 Fibre interactions with compounds

This research has confirmed earlier findings that the extent to which odours are retained and desorbed by clothing, following laundering, depends largely on inherent fibre type that the clothing is made from (McQueen et al., 2008; Munk et al., 2001). This study found that the amounts of octanoic acid and nonenal extracted from cotton to be significantly lower than that extracted from polyester at all inoculation/wash cycles using both regular and sport detergents. Similar results were found by Munk et al., (2001) where the amounts of all six odorants (ethyl-butanoate, (Z)-4-heptenal, (E)-2-nonenal, 3-methylbutanoic acid, 4-methyloctanoic acid and guaiacol) extracted from soiled cotton fabrics were much lower than that extracted from polyester fabric following laundering. Laundering was also found to be effective in removing many of the carboxylic acids, including octanoic acids, present in cotton worn against the underarm; whereas, it was less effective at removing/reducing C4-C8 chained carboxylic acids from polyester fabrics (McQueen et al., 2014).

Although cotton may have absorbed more compounds due to its hydrophilicity, it allowed more laundry liquor to easily enter its structure and break the interactions with both octanoic acid and nonenal. In addition to the interactions between polyester and the odorants, the hydrophobicity of polyester may have also slowed down the absorbency of laundry liquor, thus leading to the lesser effect of laundry on the amount of odorants (especially nonenal) removed from polyester.

Interestingly, headspace analysis showed that despite the high absorption of octanoic acid and affinity to cotton, laundering removed more octanoic acid from cotton than from polyester. Laundering also removed more nonenal from cotton than from polyester despite the fact that nonenal was likely absorbed into the structure of the cotton fibres as compared with possibly only adsorption to the surface of polyester. It was also apparent laundering was more efficient in removing octanoic acid than removing nonenal from polyester. This suggests that the non-polar oily nonenal odorant was not being cleaned off polyester as effectively. As a result, there was a far higher accumulation of residual odorants on polyester than on cotton.

5.2.2 Effect on inoculation/wash cycles on removal of odorants from fabrics

The accumulation of odour over multiple wear/wash cycles of clothing is significantly influenced by fibre types and laundry processes. Consistent with Munk et al., (2001), and based on the amount of odorant retained in both cotton and polyester, laundering was shown more effective in removing octanoic acid from clothing fabrics and less nonenal from the same fabrics. Both detergents effectively removed octanoic acid and nonenal from cotton after one wash. There was also an accumulation of the amount of odorants retained on cotton after 5 inoculation/wash cycles; this was expected as it was suggested by Munk et al., (2001) and by McQueen et al., (2014). However, it was a surprising finding that there was no significant difference in the amount of odorants accumulated between 5 and 10 inoculation/wash cycles as double the odorant had been applied to the fabric (an additional 5 applications) so an increase in accumulation of residual odorant was expected, as was seen between 1 and 5 cycles.

One possible explanation could relate to findings of Rhee et al., (1993) in relation to increased washing and wicking ability of fabrics. Rhee et al., (1993) found that as cotton shrunk during laundering it led to reduced contact angles and increased wicking ability of cotton due to increased pore volume. Increased wicking may explain the accumulation of odorants between 1 and 5 inoculation/wash cycles on cotton. The authors also showed that wicking rate of cotton gradually decreased as laundering increased from 5 to 10 and that after 10 laundry cycles there was no difference between washed and unwashed cotton (Rhee, Young, & Sarmadi, 1993). The dip in wicking rate may explain the decrease in the absorption of odorants in this study. In addition, an electron microscopic view of cotton showed that cotton fibrillates in water and further beating leads to an even finer splitting of the cotton strands (Hearle & Simmens, 1973). This fibrillation may have opened up the structure of cotton to allow more wash liquor to enter the cotton fibre for more effective removal of accumulated and newly sorbed odorants, leading to a reduction in residual odorants after 10 inoculation/wash cycles in this study.

There was also an accumulation of both octanoic acid and nonenal on polyester between 1 and 5 inoculation/wash cycles (direct extraction). Although there was a slight decrease in mean values after 10 cycles from 5, the difference was not significant due to high variability. This is similar to the study by Rhee et al., (1993) where laundry reduced the contact angles of polyester, resulting in significantly increased wicking rates after 5 launderings. Increased wicking suggests that more odorants may be sorbed and therefore formed a more strong adhesion with polyester. However the fact that there was no change in the amount of odorants accumulated on polyester after 10 inoculation/wash cycles in this study, it contradicts the expected increase in absorption of moisture after 10 washes as found by Rhee et al., (1993).

Unlike cotton fibre, polyester fibre has the ability to resist abrasion, and it is comparably difficult to fibrillate during laundry, so an increase in accumulation was expected (Fangueiro et al., 2008; Hearle & Simmens, 1973). The contradiction may be attributed to the fact that Rhee et al., examined laundry and the effect of finishes on textile materials, not textiles soiled with odorants, so the effects of odorants were not examined. The odorants in this study may have accumulated on polyester between 1 and 5 cycles and have reached a saturation point where no more of the odorants could be absorbed further, or formed a layer or film on the surface of polyester, disallowing any more ad/absorption of odorants. Nevertheless, it is important to state that there is still a lot unknown about why there was not a significant increase in accumulation; further research needs to be conducted to help determine what mechanisms are at play.

McQueen et al, (2014), who first discussed the accumulation of odorants in textile materials, had similar results. However, based on their findings, accumulation was expected to continue as wear and wash continued. In contrast, the findings in the current study showed no significant increase between 5 and 10 cycles. This may be because McQueen et al, (2014) only performed chemical analysis after 20 washes, by which time the accumulation might have reached its threshold or saturation, without any significant change. The current study thus gives a gradual overview or insight into the dynamism of odour retention and accumulation following washing over a long period of time.

5.2.3 Effect of detergents on removal of odorants

This study showed that there was no apparent difference between regular and sport detergent in removing odorants from clothing, which was unexpected. The only significant difference was in the amount of octanoic acid extracted from cotton, where the mean of regular detergent ranges from 3.71 to 8.36 (log mean = 0.89) was lower than sport detergent ranges from 11.64 to 26.00 (log mean = 1.34).

One possible explanation for this result could be that there may have been an interaction between the extra elements (Fragrances and Alcohols, C16-18, ethoxylated) in sports detergents and the other ingredients which caused the sport detergent to perform unexpectedly against the regular detergent. Research showed that the right selection of ingredients and surfactants is necessary for an optimum detergency. An equal amount of anionic and cationic surfactant was shown to be not as effective, as they neutralize to form a salt that acts like an additional greasy soil. However, a little amount of specific cationic surfactant to anionic or nonionic surfactant can greatly enhance detergency performance (Smulders & Sung, 2012). Although both detergents have anionic (benzenesulfonate) and nonionic (alcohol ethoxylates) surfactants together as part of their ingredients, the amounts and ratio are not known (Household products database, 2017). Therefore, the evaluation of the ingredients and surfactants were not attempted in this study, but would be very helpful in future studies.

It could also be that the regular (free and gentle) detergent is prepared with more concentrated amounts of the basic effective ingredients than the sports detergent is, perhaps to make up for the absence of perfume. However, it must be noted that this experiment was conducted under laboratory conditions and may not have taken account of several real-world variables such as the storage of clothing in a gym bag or air drying before washing. In addition, only two odorants (octanoic acid and nonenal) were examined on clean fabrics and therefore the mixture of sebum, other soils and odorants were not taken into account.

Chapter 6

Summary, conclusions and recommendations

6.1 Summary

The purpose of this study was to investigate the ad/absorption and desorption of odorous compounds by cotton and polyester fabrics, before and after 10 cycles (simulating use and laundry), and the efficiency of two selected detergents in the accumulation of residual odorants.

Octanoic acid and nonenal were dissolved together in dichloromethane and inoculated onto cotton and polyester fabrics and left to stand for 24 hours. The volatiles released in the headspace above the fabrics were measured using an SPME fibre for 22 hours and analysed on a GC-FID instrument. The odorants remaining in the fabric were then directly extracted using dichloromethane and concentrated and 1µl of the concentrated extract was analysed using the GC-FID instrument. Total peak areas were higher for polyester than for cotton following headspace analysis with the SPME fibre. Following direct extraction, cotton ad/absorbed more octanoic acid than polyester did and polyester ad/absorbed more nonenal than cotton did.

Cotton and polyester fabric specimens were subjected to repeated inoculation/wash cycles with two different detergents. The experimental design was a 2 x 2 x 2 x 3 factorial design where the independent variables included 2 chemical odorants (octanoic acid, nonenal), 2 fibres (cotton, polyester), 2 detergents (regular, sport) and 3 inoculation/wash cycles (1, 5, 10). The same procedure described above for measuring headspace volatiles and compounds retained within the fabric on unwashed fabrics samples was conducted for inoculated and washed fabrics. An accumulation of odorants between 1 and 5 inoculation/wash cycles was apparent for both cotton and polyester fabrics. However, after 10 cycles, when compared to after 5 cycles, lower or not significantly different quantities of odorants were extracted or detected in the headspace. The two detergents used in laundry generally did not influence the removal of odorants, except that regular detergent was more efficient than sport detergent in removing octanoic acid from cotton.

6.2 Conclusions

The findings of this study are limited to the odorants, fabrics, detergents and experimental conditions of the current research. However, based on the results the following conclusions can be made:

1. The sorption of chemical odorants in cotton and polyester fabrics prior to washing was greatly influenced by the physio-chemical properties of the textiles and odorants as:
    - cotton sorbs greater quantities of octanoic acid than polyester.
    - polyester sorbs greater quantities of nonenal than cotton.
2. However, the desorption of chemical odorants from cotton and polyester fabrics as detected by headspace analysis, using SPME fibres, may be influenced more by the textile properties, than the properties of the chemical odorants as:
    - cotton released less of both octanoic acid and nonenal compounds into the headspace as compared with polyester.
3. Laundering is effective in removing odorants from fabrics. However, the physio-chemical properties of the textile fabric and chemical odorant are <u>both</u> important as:
    - the polar octanoic acid was more easily removed from both fabrics than the non-polar nonenal. Octanoic acid was more effectively removed from cotton than from polyester even though octanoic acid has a greater affinity to, and was absorbed more, by cotton than by polyester;
    - nonenal was more effectively removed from cotton than it was from polyester despite the fact that it is oily and more easily sorbed into the fibre structure of cotton than the sorption onto the surface of polyester;

- the non-polar nonenal was difficult to remove from the non-polar hydrophobic polyester by washing, resulting in higher quantities of nonenal compared with octanoic acid in the head-space.

6.3 Recommendations

The following recommendations are made for better understanding the interactions between odorous compounds and textile materials based on the findings and limitations in the current study:

1. The peak heights and area of odorous compounds may not necessarily represent the intensity of odorants sorbed or desorbed by textile materials. Knowing the concentrations of odorants can better represent the intensity of odorants. The concentration of odorants can be calculated using a calibration curve.

2. Dodecane was used as an internal standard in this study to aid in normalising data. However, dodecane and octanoic acid behaved unexpectedly as they may have had some odd interactions with the test fabrics and laundering. A more suitable alkane that will not only interact well with other compounds and GC but will also interact better with clothing and laundry process should be used as the internal standard.

3. Laundry does have an effect on the physio-chemical properties of textile materials. More investigations into the physio-chemical properties of textile materials (including wool, nylon) with residual odour are needed to give a better insight into the build-up of odour in fibre structures.

4. Detergents from the same manufacturer were used in this study. Although there are some differences in the ingredients used, the basic ingredients were likely the same, and this may be the reason for the minimal differences between the efficiencies of the two detergents. Similar to the study where the survival of microbes was examined, using the

US and European detergents (Munk et al., 2001), when detergents from different manufacturers are used, there could be very apparent differences due to possibly different technologies and ingredients. Analysis of the chemistry of detergents will also be very insightful for such a study.

5. Cotton and polyester clearly showed different behaviours in the sorption of odorants with cotton absorbing more acids than nonenal due to its hydrophilicity while polyester does the inverse due to its hydrophobic nature. Cotton and polyester blend was valued at over USD 7 billion in 2016 alone (Industry Analysis, 2017) therefore it will be worthy to investigate this interesting interaction between odorants and cotton/polyester blends.

References

Agrawal, K., & Jassal, Ma. (2008). Manufacture of polyamide fibres. In *Polyester and Polyamides*, 97–139. doi.org/10.1533/9781845694609.1.97

Ara, K., Hama, M., Akiba, S., Koike, K., Okisaka, K., Hagura, T., … Tomita, F. (2006). Foot odor due to microbial metabolism and its control. *Canadian Journal of Microbiology*, *52*, 357–364. doi.org/10.1139/W05-130

Bajpai, D., & Tyagi, V. K. (2007). Laundry detergents: an overview. *Journal of Oleo Science*, *56*(7), 327–340. doi.org/10.5650/jos.56.327

Bartels, V. T. (2005). Physiological comfort of sportswear. *Textiles in Sport*, 177–203. doi.org/10.1533/9781845690885.3.177

Bernier, U. R., Kline, D. L., Schreck, C. E., Yost, R. A., & Barnard, D. R. (2002). Chemical analysis of human skin emanations: comparison of volatiles from humans that differ in attraction of Aedes aegypti (Diptera: Culicidae). *Journal of the American Mosquito Control Association*, *18*(3), 186–95.

Bowers, C. A., & Chantrey, G. (1969). Factors controlling the soiling of white polyester cotton fabrics part i: laboratory studies. *Textile Research Journal*, *39*(1), 1–11.

Brotherhood, J. R. (2008). Heat stress and strain in exercise and sport. *Journal of Science and Medicine in Sport / Sports Medicine Australia*, *11*(1), 6–19. doi.org/10.1016/j.jsams.2007.08.017

Callewaert, C., De Maeseneire, E., Kerckhof, F. M., Verliefde, A., Van de Wiele, T., & Boon, N. (2014). Microbial odor profile of polyester and cotton clothes after a fitness session. *Applied and Environmental Microbiology*, *80*(21), 6611–6619.

doi.org/10.1128/AEM.01422-14

Cantergiani, E., & Benczédi, D. (2002). Use of inverse gas chromatography to characterize cotton fabrics and their interactions with fragrance molecules at controlled relative humidity. *Journal of Chromatography A*, *969*(1–2), 103–110. doi.org/10.1016/S0021-9673(02)00380-1

Celanese, A. (2001). Complete textile glossary. *Fibre Dictionary*, *5*, 1–209. doi.org/10.1017/CBO9781107415324.004

Chern, C.-S., Lin, S.-Y., Chen, L.-J., & Wu, S.-C. (1997). Emulsion polymerization of styrene stabilized by mixed anionic and nonionic surfactants. *Polymer*, *38*(8), 1977–1984.

Chung, H., & Seok, H. J. (2012). Populations of malodor-forming bacteria and identification of volatile components in triolein-soiled cotton fabric. *Fibers and Polymers*, *13*(6), 740–747. doi.org/10.1007/s12221-012-0740-5

Curran, A. M., Rabin, S. I., Prada, P. A., & Furton, K. G. (2005). Comparison of the volatile organic compounds present in human odor using SPME-GC/MS. *Journal of Chemical Ecology*, *31*(7), 1607–1619. doi.org/10.1007/s10886-005-5801-4

Das, A. &, & Alagirusamy, R. (2010). Moisture transmission. In *Science in Clothing Comfort* (106–135).

Das, A., Kothari, V., Fangueiro, R., & Araújo, M. De. (2007). Moisture Transmission through textiles Part II : evaluation methods and mathematical modelling. *AUTEX Research Journal*, *7*, 194–216.

Decréau, R. A., Marson, C. M., Smith, K. E., & Behan, J. M. (2003). Production of malodorous steroids from androsta-5,16-dienes and androsta-4,16-dienes by Corynebacteria and other human axillary bacteria. *The Journal of Steroid Biochemistry and Molecular Biology*, *87*(4), 327–336. doi.org/10.1016/j.jsbmb.2003.09.005

Dravnieks, A., Krotoszynski, B. K., Lieb, W. E., & Jungermann, E. (1968). Influence of an antibacterial soap on various effluents from axillae. *Journal of the Society of Cosmetic Chemists*, *19*(9), 611–626.

Easley, C. B., Laughlin, J. M., Gold, R. E., & Schmidt, K. (1982). Detergents and water temperature as factors in methyl parathion removal from denim fabrics 1. *Bulletin Environmental Contamination Toxicology*, *28*, 239–244.

East, A. J. (2005). Polyester fibres, *Synthetic Fibres: Nylon, Polyester, Acrylic, Polyolefin* (95–166). Cambridge: Woodhead Publishing Limited.

Emter, R., & Natsch, A. (2008). The sequential action of a dipeptidase and a beta-lyase is required for the release of the human body odorant 3-methyl-3-sulfanylhexan-1-ol from a secreted Cys-Gly-(S) conjugate by Corynebacteria. *The Journal of Biological Chemistry*, *283*(30), 20645–52. doi.org/10.1074/jbc.M800730200

Fangueiro, R., Gonilho Pereira, C., & De Araújo, M. (2008). Applications of polyesters and polyamides in civil engineering. *Polyesters and Polyamides*, 542–592. doi.org/10.1533/9781845694609.3.542

Fibre2fashion, C. (2017). (Fibre2fashion, August 2017). Retrieved from: http://www.fibre2fashion.com/industry-article/7901/global-polyester-market-outlook-till-2020.

Gower, D. B., Holland, K. T., Mallet, A. I., Rennie, P. J., & Watkins, W. J. (1994). Comparison of 16-Androstene steroid concentrations in sterile apocrine sweat and axillary secretions: interconversions of 16-Androstenes by the axillary microflora-a mechanism for axillary odour production in man? *Journal of Steroid Biochemistry and Molecular Biology*, *48*(4), 409–418. doi.org/10.1016/0960-0760(94)90082-5

Gower, D. B., Mallet, A. I., Watkins, W. J., Wallace, L. M., & Calame, J. P. (1997). Capillary gas chromatography with chemical ionization negative ion mass spectrometry in the identification of odorous steroids formed in metabolic studies of the sulphates of androsterone, DHA and 5-androst-16-en-3-ol with human axillary bacterial iso. *Journal of Steroid Biochemistry and Molecular Biology*, *63*(1–3), 81–89. doi.org/10.1016/S0960-0760(97)00075-7

Gozu, Y., Haze, S., N., Akamura, S., Kohno, Y., Fukui, H., Kumano, Y., … Yamazaki, K. (2000). Development of care-products to prevent aged body odor. *Journal of the Society of Cosmetic Chemists.*, 379–386.

Greene, R. S., Downing, D. T., Pochi, P. E., & Strauss, J. S. (1970). Anatomical variation in the amount and composition of human skin surface lipid. *Journal of Investigative Dermatology*, *54*(3), 240–247. doi.org/10.1111/1523-1747.ep12280318

Hamada, K., Haruyama, S., Yamaguchi, T., Yamamoto, K., Hiromasa, K., Yoshioka, M., … Nakamura, M. (2014). What determines human body odour? *Experimental Dermatology*, *23*(5), 316–317. doi.org/10.1111/exd.12380

Hammer, T. R., Berner-Dannenmann, N., & Hoefer, D. (2013). Quantitative and sensory evaluation of malodour retention of fibre types by use of artificial skin, sweat and radiolabelled isovaleric acid. *Flavour and Fragrance Journal*, *28*(4), 238–244. doi.org/10.1002/ffj.3134

Hämmerle, F. M. (2011). The cellulose gap. *Lenzinger Berichte*, *89*, 12–21.

Hasegawa, Y., Yabuki, M., & Matsukane, M. (2004). Identification of new odoriferous compounds in human axillary sweat. *Perspectives in Flavor and Fragrance Research*, *1*, 215–223. http://doi.org/10.1002/9783906390475.ch18

Havenith, G., Bröde, P., den Hartog, E., Kuklane, K., Holmer, I., Rossi, R. M., … Wang, X. (2013). Evaporative cooling: effective latent heat of evaporation in relation to evaporation distance from the skin. *Journal of Applied Physiology (Bethesda, Md. : 1985)*, *114*

Haze, S., Gozu, Y., Nakamura, S., Kohno, Y., Sawano, K., Ohta, H., & Yamazaki, K. (2001). 2-Nonenal newly found in human body odor tends to increase with aging. *Journal of Investigative Dermatology*, *116*(4), 520–524.

Hearle, J. W. S., & Simmens, S. C. (1973). Electron microscope studies of textile fibres and materials. *Polymer*, *14*, 273–285.

Hites, A. R. (1997). Gas Chromatography Mass Spectrometry. *Handbook of Instrumental Techniques for Analytical Chemistry* (pp. 609–626).

Household Products Database. (2017). Retrieved from https://householdproducts.nlm.nih.gov/. doi.org/10.1080/00405167.2011.573240

Illman, J. C., Albin, T. B., & Stupel, H. (1972). Studies on replacement of phosphate builders in laundry detergents using radiolabeled soils. *Journal of the American Oil Chemists' Society*, *49*(4), 217–221. doi.org/10.1007/BF02582581

Industry Anaysis. (2017). Retrieved from https://www.gminsights.com/industry-analysis/blended-fibres-market.

James, A. G., Cox, D., & Worrall, K. (2013). Microbiological and biochemical origins of human foot malodour. *Flavour and Fragrance Journal*. http://doi.org/10.1002/ffj.3136

James, A. G., Hyliands, D., & Johnston, H. (2004). Generation of volatile fatty acids by axillary bacteria 1. *International Journal of Cosmetic Science*, *26*, 149–156.

Kadolph, S. J. (2010). *Textiles*. doi.org/10.1177/0887302X07303625

Kanda, F., Yagi, E., Fukuda, M., Nakajima, K., Ohta, T., & Nakata, O. (1990). Elucidation of chemical compounds responsible for foot malodour. *British Journal of Dermatology*, *122*(6), 771–776. doi.org/10.1111/j.1365-2133.1990.tb06265.x

Kanlayavattanakul, M., & Lourith, N. (2011). Body malodours and their topical treatment agents. *International Journal of Cosmetic Science*, *33*(4), 298–311. doi.org/10.1111/j.1468-2494.2011.00649.x

Kay Obendorf, S., & Webb, J. J. (1987). Detergency study: distribution of natural soils on shirt collars. *Textile Research Journal*, *57*(10), 557–563. doi.org/10.1177/004051758705701001

Kenneth K. Andersen, & David T. Bernstein. (1975). Some chemical constituents of the scent of the striped skunk (Mephitis mephitis) 1. *Journal Chemical Ecology., 1*(4), 493–499.

Kim, C. J., Stone, J. F., & Sizer, C. E. (1982). Removal of pesticide residues as affected by laundering variables. *Bulletin Environmental Contamination and Toxicology*, *29*, 95–100.

Kissa, E. (1996). Wetting wicking. *Textile Research Journal*, *66*(10), 660–668.

Kongkachuichay, P., Shitangkoon, A., & Chinwongamorn, N. (2002). Studies on dyeing of silk yarn with lac dye: *Science Asia*, *28*, 161–166.

Kothari, V. K. (2008). Polyester and polyamide fibres – apparel applications. *Polyesters and Polyamides*, 419–440. doi.org/10.1533/9781845694609.3.419

Krishnan, P. S. G., & Kulkarni, S. T. (2008). Polyester resins. *Journal of the Franklin Institute*, *270*, 62. doi.org/10.1016/0016-0032(60)90918-2

Kubota, H., Mitani, A., Niwano, Y., Takeuchi, K., Tanaka, A., Yamaguchi, N., & Kawamura, Y. (2012). Moraxella species are primarily responsible for generating malodor, 3317–3324. doi.org/10.1128/AEM.07816-11

Lee, S. M., Papathakis, M. L., Feng, H.-M. C., Hunter, G. F., & Carr, J. E. (1991). Multipesticide residue method for fruits and vegetables: California department of food and agriculture. *Journal of Analytical Chemistry*, *339*, 376–383.

Leidal, R., Rapini, R., Sato, F., Ung, H., & Sato, K. (1982). Evolution and development of human axillary sweat glands. *Journal of Investigative Dermatology*, *78*(4), 352–352. doi.org/10.1111/j.1556-4029.2009.01236.x

Leidreiter, H. I., Gruning, B., & Kaseborn, D. (1997). Amphoteric surfactants: processing, product composition and properties. *International Journal of Cosmetic Science*, *19*(5), 239–253. doi.org/10.1111/j.1467-2494.1997.tb00187.x

Linke, D. (2009). Detergents. an overview. *Methods in Enzymology* (463). Elsevier Inc. doi.org/10.1016/S0076-6879(09)63034-2

Liu, H., Obendorf, S. K., Leonard, M. J., Young, T. J., & Incorvia, M. J. (2005). Adsorption of aroma chemicals on cotton fabric from aqueous systems. *Journal of Surfactants and Detergents*, *8*(4), 311–317. doi.org/10.1007/s11743-005-0361-3

Liu, R., & Little, T. (2009). The 5Ps model to optimize compression athletic wear comfort in sports. *Journal of Fiber Bioengineering and Informatics*, *2*(1), 41–52. doi.org/10.3993/jfbi06200907

Lloyd, J., & Adams, C. (1989). Domestic laundering of textiles. *Textile*, *18*(3), 72–82.

Manshahia M, & Das A. (2014). High active sportswear – a critical review. *Indian Journal of Fibre & Textile Research*, *39*, 441–449.

McCall, E. R., & Jurgens, J. F. (1951). Chemical composition of cotton. *Textile Research Journal*, *21*(1), 19–21. doi.org/10.1177/004051755102100105

McQueen, R. H., Harynuk, J. J., Wismer, W. V., Keelan, M., Xu, Y. &, & Paulina de la Mata, A. (2014). Axillary odour build-up in knit fabrics following multiple use cycles. *International*

Journal of Clothing Science and Technology, *26*(4), 274–290. doi.org/10.1108/IJCST-05-2013-0064

McQueen, R. H., Laing, R. M., Brooks, H. J. L., & Niven, B. E. (2007). Odor intensity in apparel fabrics and the link with bacterial populations. *Textile Research Journal*, *77*(7), 449–456. doi.org/10.1177/0040517507074816

McQueen, R. H., Laing, R. M., Delahunty, C. M., Brooks, H. J. L., & Niven, B. E. (2008). Retention of axillary odour on apparel fabrics. *Journal of the Textile Institute*, *99*(6), 515–523. doi.org/10.1080/00405000701659774

McQueen, R. H., Laing, R. M., Wilson, C. A., Niven, B. E., & Delahunty, C. M. (2007). Odor Retention on apparel fabrics: development of test methods for sensory detection. *Textile Research Journal*, *77*(9), 645–652. doi.org/10.1177/0040517507078792

Moat, A. G., & Foster, J. W. (1988). Carbohydrate metabolism and energy production. *Microbial Physiology*, *2*, 118–220.

Munk, S., Johansen, C., Stahnke, L. H., & Adler-Nissen, J. (2001). Microbial survival and odor in laundry. *Journal of Surfactants and Detergents*, *4*(4), 385–394. doi.org/10.1007/s11743-001-0192-2

Munk, S., Münch, P., Stahnke, L., Adler-Nissen, J., & Schieberle, P. (2000). Primary odorants of laundry soiled with sweat/sebum: influence of lipase on the odor profile. *Journal of Surfactants and Detergents*, *3*(4), 505–515. /doi.org/10.1007/s11743-000-0150-z

Natsch, A., Schmid, J., & Flachsmann, F. (2004). Identification of odoriferous sulfanylalkanols in human axilla secretions and their formation through cleavage of cysteine precursors by a C-S lyase isolated from axilla bacteria. *Chemistry & Biodiversity*, *1*(7), 1058–1072.

Obendorf, S. K., Namaste, Y. M. N., & Durnam, D. J. (1983). A microscopical study of residual oily soil distribution on fabrics of varying fiber content. *Textile Research Journal*, *53*(6), 375–383. doi.org/10.1177/004051758305300609

Obendorf, S. K., & Webb, J. J. (1987). Detergency study: distribution of natural soils on shirt collars. *Textile Research Journal*, *57*(10), 557–563. doi.org/10.1177/004051758705701001

Okubo, M., Saeki, N., & Yamamoto, T. (2008). Development of functional sportswear for controlling moisture and odor prepared by atmospheric pressure nonthermal plasma graft polymerization induced by RF glow discharge. *Journal of Electrostatics*, *66*(7–8), 381–387. doi.org/10.1016/j.elstat.2008.03.003

Patnaik, A., Rengasamy, R. S., Kothari, V. K., & Ghosh, A. (2006). Wetting and wicking in fibrous materials. *Textile Progress*, *38*(1), 1–105. doi.org/10.1533/jotp.2006.38.1.1

Pattanaik, M, N., & Ray, S, C. (2014). A Study on the effect of crease resistant finish treatment on perspiration fastness property of cotton garments. *International Journal of Textile Science*, *3*(1), 1–6. doi.org/10.5923/j.textile.20140301.01

Pause, B. (1996). Measuring the water vapor permeability of coated fabrics and laminates. *Journal of Coated Fabrics*, *25*, 311–320.

Prada, P. A., Curran, A. M., & Furton, K. G. (2011). The evaluation of human hand odor volatiles on various textiles: a comparison between contact and noncontact sampling methods. *Journal of Forensic Sciences*, *56*(4), 866–881. doi.org/10.1111/j.1556-4029.2011.01762.x

Prahsarn, C. (2005). Moisture vapor transport behavior of polyester knit fabrics. *Textile Research Journal*, *75*(4), 346–351. doi.org/10.1177/0040517505053811

Rennie, P. J., Gower, D. B., & Holland, K. T. (1991). In-vitro and in-vivo studies of human axillary odour and the cutaneous microflora. *The British Journal of Dermatology*, *124*(6), 596–602. doi.org/10.1111/j.1365-2133.1991.tb04958.x

Rennie, P. J., Gower, D. B., Holland, K. T., Mallet, A. I., & Watkins, W. J. (1990). The skin microflora and the formation of human axillary odour. *International Journal of Cosmetic Science*, *12*(5), 197–207. doi.org/10.1111/j.1467-2494.1990.tb00535.x

Rhee, H., Young, R. A., & Sarmadi, A. M. (1993). The effect of functional finishes and laundering on textile materials part ii: characterization of liquid flow. *Textile Institute*, *84*(3), 406–418.

Richter, T. M., Bremer, P. J., Silcock, P., & Laing, R. M. (2017). Textile binding and release of body odor compounds measured by proton transfer reaction – mass spectrometry. *Textile Research Journal*, 4051751772512. doi.org/10.1177/0040517517725126

Saini, A., Okeme, J. O., Mark Parnis, J., McQueen, R. H., & Diamond, M. L. (2016). From air to clothing: characterizing the accumulation of semi-volatile organic compounds to fabrics in indoor environments. *Indoor Air*, 1–11. doi.org/10.1111/ina.12328

Salaguer, J.-L. (2002). Surfactants types and uses. *Laboratory of Formulation, Interfaces, Rheology and Processes*, *2*, 1–49.

Scheibel, J. J. (2004). The evolution of anionic surfactant technology to meet the requirements of the laundry detergent industry. *Journal of Surfactants and Detergents*, *7*(4), 319–328. doi.org/10.1007/s11743-004-0317-7

Scheurell, D. M., Spivak, S. M., & Hollies, N. R. S. (1985). Dynamic surface wetness of fabrics in relation to clothing comfort. *Textile Research Journal*, 394–399.

Schwuger, M. J., & Smolka, H. G. (1978). Sodium-Aluminium-Silicates in the washing process - part iii. ion exchange and detergency. *Colloid and Polymer Science Kolloid-Zeitschrift & Zeitschrift fur Polymere*, *256*(10), 1014–1020. doi.org/10.1007/BF01520989

Smallegange, R. C., Verhulst, N. O., & Takken, W. (2011). Sweaty skin: an invitation to bite? *Trends in Parasitology*, *27*(4), 143–148. doi.org/10.1016/j.pt.2010.12.009

Smith, F. & Mei, W. (2013). Fashion applications for polyester fiber, particularly hydrophilic polyester. Retrieved from https://www.scribd.com/document/29734226/polyster

Smulders, E., Rähse, W., & Jakobi, G. (2007). Laundry detergents. *Ullmann's Encyclopedia of Industrial Chemistry*, 270. doi.org/10.1002/14356007.a08_315.pub2

Smulders, E., Rybinski, W., Rahse, W., Steber, J., Wiebel, F., & Nordskog, A. (2007). Laundry detergents. *Wiley-VCH Verlag GmbH & Co. KGaA.* doi.org/10.1002/14356007.a08

Smulders, E., & Sung, E. (2012). Laundry Detergents, 5. washing conditions and washing machines. *Ullmann's Encyclopedia of Industrial Chemistry*, *20*, 394–449. doi.org/10.1002/14356007.o15

Sommerville, B. a, Mccormick, J. P., & Broom, D. M. (1994). Analysis of human sweat volatiles: an example - of pattern recognition in the analysis and interpretation of gas chromatograms. *Pesticides Science*, 365–368.

Stahl, W. H. (1973). Compilation of odor and taste threshold values data. *American Society for Testing and Materials.*, (780).

Starkenmann, C., Niclass, Y., Troccaz, M., & Clark, A. (2005). Human axillary malodour: identification of the precursor of S-3-Methyl-3-Sulphanylhexan-1-ol, the sulphury malodor of human axilla sweat. *Chemistry & Biodiversity*, *2*, 705–716.

Sutanti Budikania, T., Irawan, C., Afriani, K., & Saksono, N. (2017). Degradation of Linear Alkylbenzene Sulfonate (LAS) by using multi-contact glow discharge electrolysis (m-CGDE) and Fe 2+ ion as catalyst. doi.org/10.1016/j.jece.2017.04.025

Takeuchi, K., Yabuki, M., & Hasegawa, Y. (2013). Review of odorants in human axillary odour and laundry malodour: the importance of branched C7 chain analogues in malodours perceived by humans. *Flavour and Fragrance Journal*, *28*(4), 223–230. doi.org/Doi 10.1002/Ffj.3130

Taylor, D., Daulby, A., Grimshaw, S., James, G., Mercer, J., & Vaziri, S. (2003). Characterization of the microflora of the human axilla. *International Journal of Cosmetic Science*, *25*(3), 137–45. doi.org/10.1046/j.1467-2494.2003.00181.x

Teufel, L., Pipal, A., Schuster, K. C., Staudinger, T., & Redl, B. (2010). Material-dependent growth of human skin bacteria on textiles investigated using challenge tests and DNA genotyping. *Journal of Applied Microbiology*, *108*(2), 450–61.

Thierry, A., Maillard, M., & Yvon, M. (2002). Conversion of leucine to isovaleric acid by propionibacterium freudenreichii TL 34 and ITGP23. *Applied and Environmental Microbiology*, *68*(2), 608–615. doi.org/10.1128/AEM.68.2.608

Thomas B. Aldrich. (1896). A chemical study of the secretion of the anal glands of Memphitis Memohitica (common skunk), with remarks on the physiological properties of this secretion. *The Journal of Experimental Medicine*, *1*(2), 323–340.

Tokiwa, F. &, & Moriyama, N. (1969). Mixed micelle formation of anionic and nonionic surfactants. *Journal of Colloid and Interface Sciienceence*, *3*(30), 338–344.

Troccaz, M., Benattia, F., Borchard, G., & Clark, A. J. (2008). Properties of recombinant staphylococcus haemolyticus cystathionine -lyase (metC) and its potential role in the generation of volatile thiols in axillary malodor. *Chemistry and Biodiversity*, *5*(11), 2372–2385.

Troccaz, M., Starkenmann, C., Niclass, Y., van de Waal, M., & Clark, A. J. (2004). 3-Methyl-3-sulfanylhexan-1-ol as a major descriptor for the human axilla-sweat odour profile.

Chemistry & Biodiversity, *1*(7), 1022–1035.

Velfgek, J., Davfdek, J., Hajglov~t, J., Kubelka, V., Jan~ek, G., & Mfinkovfi, B. (1978). lebensmittel- untersuchung und-forschung chlorohydrins in protein hydrolysates chlorhydrine in eiweil hydrolysaten. *Z. Lebensm Unters Forsch*, *167*, 241–244.

Venkatesh, G. M., Dweltz, N. E., Madan, G. L., & Alurkar, R. H. (1974). A study of the soiling of textiles and development of anti-soiling and soil release finishes: a review. *Textile Research Institute*, 352–362.

Water Hardness in Canada. (2016). Water hardness in Canada, 1–4. Retrieved from http://funkyfluff.ca/water hardness in canada/

Wakelyn, P. J., Bertoniere, N. R., French, A. D., Thibodeaux, D. P., Rousselle, M.-A., Triplett, B. A., … Gamble, G. R. (2006). Structural properties of cotton. *Cotton Fiber Chemistry and Technology*, 23–68. doi.org/10.1201/9781420045888.ch5

Wakelyn, P. J., Bertoniere, N. R., French, A. D., Thibodeaux, D. P., Triplett, B. A., Rousselle, M. A., ..., & Gamble, G. R. (2006). Cotton fiber chemistry and technology. *CRC Press. CRC Press*. doi.org/10.1111/j.1556-4029.2011.01762.x

Yao, L., Laing, R. M., Bremer, P. J., Silcock, P. J., & Leus, M. J. (2015). Measuring textile adsorption of body odor compounds using proton-transfer-reaction mass spectrometry. *Textile Research Journal*, *85*(17), 1817–1826. doi.org/10.1177/0040517515576325

Yoon, H. N & Buckley, A. (1984). Improved polyester. *Textile Research Institute*, *84*, 289–298.

Zeng, X.-N., Leyden, J. J., Lawley, H. J., Sawano, K., Nohara, I., & Preti, G. (1991). Analysis of characteristic odors from human male axillae. *Journal of Chemical Ecology*, *17*(7), 1469–1492.

Zeng, X. nong, Leyden, J. J., Lawley, H. J., Sawano, K., Nohara, I., & Preti, G. (1991). Analysis of characteristic odors from human male axillae. *Journal of Chemical Ecology*, *17*(7), 1469–1492.doi.org/10.1007/BF00983777

Zhu, L., & Feng, S. (2003). Synergistic solubilization of polycyclic aromatic hydrocarbons by mixed anionic-nonionic surfactants. *Chemosphere*, (53), 459–467.doi.org/10.1016/S0045-6535(03)00541-1

Appendix A

Figure A.1 Experimental daily plan

Showing each fibre type coded with Inoculation/wash code, detergent and number corresponding to its canister number and whether it's in the first batch of tests or second. Colour codes show the beginning through to when a specimen is ready for chemical analysis.

		First batch								Second batch								
			Cannisters							Cannisters								ctrlP
Days	Can1	Can2	Can3	Can4	Can5	Can6		Can7	Can8	Can9	Can10	Can11	Can12					ctrlC
1	1-P1-10r1	1-C1-10r1	1-ctrlP	1-ctrlC-CO														
2	1-P2-10r1	1-C2-10r1	1-ctrlC	1-ctrlP-CO														
3	2-P1-10r1	2-C1-10r1	1-P1-10r2	1-C1-10r2	1-P1-5r1	1-C1-5r1		P1-1r1	C1-1r1	2-ctrlP	2-ctrlC-CO							
4	2-P2-10r1	2-C2-10r1	1-P2-10r2	1-C2-10r2	1-P2-5r1	1-C2-5r1		P2-1r1	C2-1r1	2-ctrlC	2-ctrlP-CO							
																End of washing and inoclation		
5	3-P1-10r1	3-C1-10r1	2-P1-10r2	2-C1-10r2	1-P1-10r3	1-C1-10r3		2-P1-5r1	2-C1-5r1	1-P1-5r2	1-C1-5r2	3-ctrlP			**1-P2-10r1**	# of wash cycles		
6	3-P2-10r1	3-C2-10r1	2-P2-10r2	2-C2-10r2	1-P2-10r3	1-C2-10r3		2-P2-5r1	2-C2-5r1	1-P2-5r2	1-C2-5r2	3-ctrlC			**1-P2-10r1**	Fabric (P-polyester, C-cotton)		
7				Break											**1-P2-10r1**	Detergent #		
8	4-P1-10r1	4-C1-10r1	3-P1-10r2	3-C1-10r2	2-P1-10r3	2-C1-10r3		3-P1-5r1	3-C1-5r1	2-P1-5r2	2-C1-5r2	1-P1-5r3	1-C1-5r3		**1-P2-10r1**	Wash level		
9	4-P2-10r1	4-C2-10r1	3-P2-10r2	3-C2-10r2	2-P2-10r3	2-C2-10r3		3-P2-5r1	3C2-5r1	2-P2-5r2	2-C2-5r2	1-P2-5r3	1-C2-5r3		**1-P2-10r1**	replicate #		
															ctrlC	Control		
10	5-P1-10r1	5-C1-10r1	4-P1-10r2	4-C1-10r2	3-P1-10r3	3-C1-10r3		4-P1-5r1	4-C1-5r1	3-P1-5r2	3-C1-5r2	2-P1-5r3	2-C1-5r3		**1-ctrlC-CO**	Carry over (Odorants)		
11	5-P2-10r1	5-C2-10r1	4-P2-10r2	4-C2-10r2	3-P2-10r3	3-C2-10r3		4-P2-5r1	4-C2-5r1	3-P2-5r2	3C2-5r2	2-P2-5r3	2-C2-5r3					
12	6-P1-10r1	6-C1-10r1	5-P1-10r2	5-C1-10r2	4-P1-10r3	4-C1-10r3		5-P1-5r1	5-C1-5r1	4-P1-5r2	4-C1-5r2	3-P1-5r3	3-C1-5r3					
13	6-P2-10r1	6-C2-10r1	5-P2-10r2	5-C2-10r2	4-P2-10r3	4-C2-10r3		5-P2-5r1	5-C2-5r1	4-P2-5r2	4-C2-5r2	3-P2-5r3	3C2-5r3					
14				Break														
15	7-P1-10r1	7-C1-10r1	6-P1-10r2	6-C1-10r2	5-P1-10r3	5-C1-10r3		5-P1-5r2	5-C1-5r2	4-P1-5r3	4-C1-5r3	4-ctrlP	1-ctrlP					
16	7-P2-10r1	7-C2-10r1	6-P2-10r2	6-C2-10r2	5-P2-10r3	5-C2-10r3		5-P2-5r2	5-C2-5r2	4-P2-5r3	4-C2-5r3	4-ctrlC	1-ctrlC					
17	8-P1-10r1	8-C1-10r1	7-P1-10r2	7-C1-10r2	6-P1-10r3	6-C1-10r3		5-P1-5r3	5-C1-5r3	5-ctrlP	1-ctrlP-CO							
18	8-P2-10r1	8-C2-10r1	7-P2-10r2	7-C2-10r2	6-P2-10r3	6-C2-10r3		5-P2-5r3	5-C2-5r3	5-ctrlC	1-ctrlC-CO							
19	9-P1-10r1	9-C1-10r1	8-P1-10r2	8-C1-10r2	7-P1-10r3	7-C1-10r3		P1-1r2	C1-1r2	6-ctrlP	2-ctrlP-CO							
20	9-P2-10r1	9-C2-10r1	8-P2-10r2	8-C2-10r2	7-P2-10r3	7-C2-10r3		P2-1r2	C2-1r2	6-ctrlC	2-ctrlC_CO							
21				Break														
22	10-P1-10r1	10-C1-10r1	9-P1-10r2	9-C1-10r2	8-P1-10r3	8-C1-10r3	7-ctrlP											
23	10-P2-10r1	10-C2-10r1	9-P2-10r2	9-C2-10r2	8-P2-10r3	8-C2-10r3	7-ctrlC											
24			10-P1-10r2	10-C1-10r2	9-P1-10r3	9-C1-10r3	8-ctrlP											
25			10-P2-10r2	10-C2-10r2	9-P2-10r3	9-C2-10r3	8-ctrlC											
26					10-P1-10r3	10-C1-10r3	9ctrlP											
27					10-P2-10r3	10-C2-10r3	9-ctrlC											
28				Break														
29					P1-1r3	C1-1r3	10-ctrlP											
30					P2-1r3	C2-1r3	10-ctrlC											

Appendix B

Laundering equipment and test parameters.

The test method for colourfastness was adopted with some modification using the Launder-O-meter (CAN/CGSB-4.2 No. 19.2-2003/ ISO 105-C06:1994). The Launder-O-meter by Atlas Electric Devices (Illinois, USA) allows up to 12 samples to be washed at the same time with possibly different wash solutions. It is known to give a good simulation of and be a standard for washing cycles of textiles for both domestic and commercial purposes (Pattanaik & Ray 2014).

Instead of “Tide® Compact Original Scent” required by the standard test methods, Tide® Free & Gentle Liquid detergent (a non-perfume version) was used similarly to a study by McQueen et al., (2014). Tide® Sport Febreze Liquid detergent was also used as it is marketed to have Febreze freshness sport active that provides better odour fighting power and deeper cleaning than Tide® Original. The company website also mentions that it contains renewing freshness technology that releases into clothing for a fresh burst of fragrance (Tide.com). Both detergents are products of Proctor & Gamble Co. (Ohio, USA). Furthermore, both detergents have anionic (benzenesulfonate) and nonionic (alcohol ethoxylates) surfactant together as part of their ingredients, but the amounts and ratio were not available (Household products database, 2017). In addition, sodium hypochlorite is required in the colourfastness tests but was not added in the wash solution as it dissolves in water into a bleaching agent which may interfere in the analysis of the study (Sodium hypochlorite, July 2016).

Regular tap water was used instead of grade-3 water specified by the Launder-O-meter test standard. The liquor ratio was 5 mL of detergent per 1 litre of water. Duration of 45 minutes of washing is required in the standard can be equated to 5 wash cycles of domestic laundry so the machine was stopped after 10 minutes to represent 1 wash cycle, before drying the fabric and prepared for the next inoculation or GC analysis. Instead of using the Launder-O-meter to increase the temperature to 30 °C as stated in the method, a stock of the wash liquor was prepared and kept constantly at 30 °C and 450 mL was poured out for each canister.

Appendix C

Calibration of standard solution

The direct extraction of octanoic acid and nonenal was determined from the calibration curve of standard solutions (see Figure C1 & C2 respectively). The calibration curves for standard solutions were linear for 0.01 ppm/10 ml to 250 ppm/10 ml of octanoic acid inoculated and 0.01ppm/10ml to 250 ppm/10 ml for nonenal. The least squares linear regression equation for standard solutions are:

Octanoic acid: $y=463.3x+196.76$ ($r= 0.9983$),

Nonenal: $y=151.4x-375.12$ ($r=0.9933$).

Where: y= Concentration of odorants

x= Area count/ Area internal standard

r= Pearson correlation coefficient.

Table C1 Calculations for concentrations (ppm) of octanoic acid and the resultant peak areas for calibration curve

Conc.#	Conc.	$C_1V_1=C_2V_2$				Solvent to make up (ml)	Peak area	std
		C_1 (ppm)	C_2 (ppm)	V_2 (ml)	V_1(ml) $=\frac{C2V2}{C2}$			
1	500						137229.8	25442.68
2	250	500	250	10	5	5	118982.9	5307.15
3	200	250	200	10	8	2	88391.37	2445.98
4	100	200	100	10	5	5	46641.6	1848.31
5	5	100	5	10	0.5	9.5	3757.33	49.79
6	1	5	1	10	2	8	501.97	48.13
7	0.1	1	0.1	10	1	9	63.8	3.15
8	0.01	0.1	0.01	10	1	9	7.8	0.1

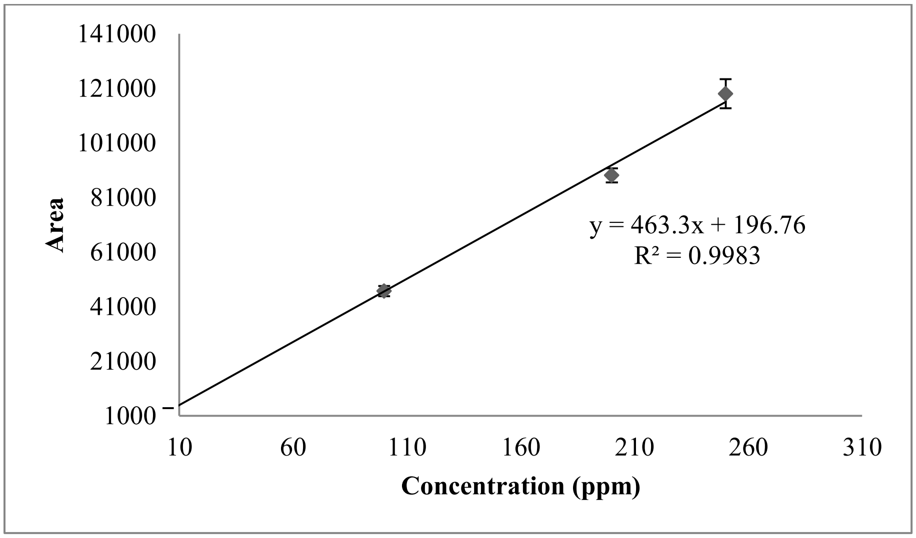


Figure C1 Calibration curve for direct extraction of octanoic acid from cotton and polyester

Table C2 Calculations for concentrations (ppm) of nonenal and the resultant peak areas for calibration curve

Conc. #	Conc.	$C_1V_1=C_2V_2$				Solvent (ml)	Peak area	std
		C_1 (ppm)	C_2 (ppm)	V_2 (ml)	V_1(ml) $=\frac{C2V2}{C2}$			
1	250	500	250	10	5	5	39380.88	2352.14
2	200	250	200	10	8	2	27531.07	987.22
3	100	200	100	10	5	5	14916.63	949.55
4	50	100	50	10	5	5	6843.3	595.37
5	5	50	5	10	1	9	400.73	5.60
6	1	5	1	10	2	8	46.67	0.25
8	0.1	0.1	0.01	10	1	9	3.23	0.42

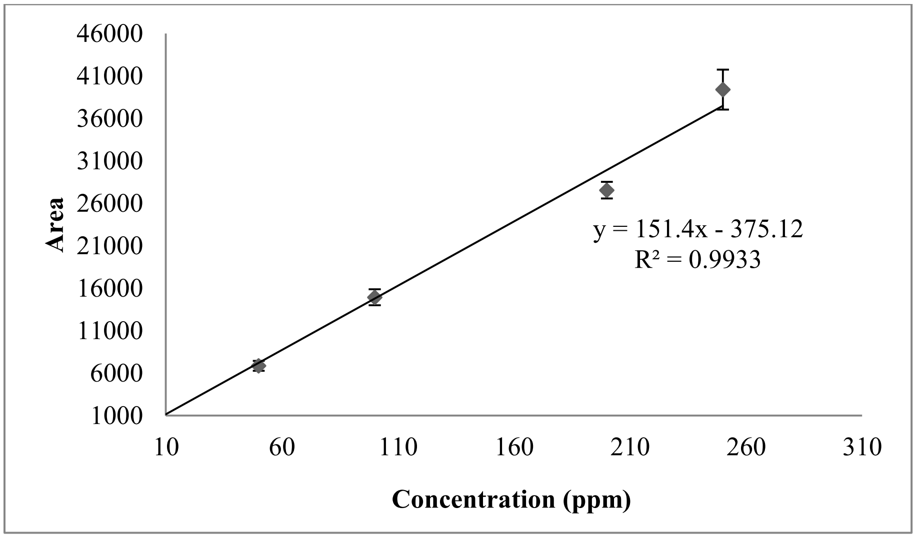


Figure C2 Calibration curve for direct extraction of nonenal from cotton and polyester